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# ARPA Coupling Program on Stress-Corrosion Cracking

## Final Technical Report: Second Edition

B. F. BROWN

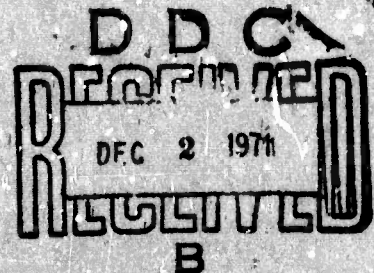
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## ABSTRACT

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## PROBLEM STATUS

This is a final technical report.

## AUTHORIZATION

NRL Problem M04-08A  
ARPA Order No. 878

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# ARPA COUPLING PROGRAM ON STRESS-CORROSION CRACKING

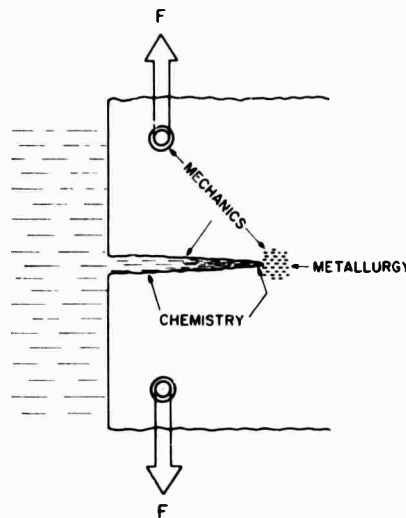
## Final Technical Report

### INTRODUCTION

#### History

By 1966 the phenomenon of SCC had affected all the military services (and NASA); had caused serious surprises to the designers of aircraft, submersibles, and rockets; and had involved all three major families of high strength structural alloys—titanium, steels, and aluminum. The Advanced Research Projects Agency (ARPA) of the Department of Defense recognized both the military importance of the problem and its technical complexity, compounding as it does the difficulties of the brittle fracture problem with chemical reactions occurring inside inaccessible cracks (Fig. 1). ARPA also was aware of new developments in surface physics and surface chemistry, some of which might be expected ultimately to afford advances in the science of metallic corrosion. ARPA therefore asked the Naval Research Laboratory to organize an intensive attack on the problem of the SCC of high-strength structural alloys with provision for coupling science to technology and also for coupling academic laboratories with an industrial laboratory and a government laboratory.

Fig. 1 - The three scientific elements of stress-corrosion cracking. Progress requires attention to all three.



#### Organization

The principal member institutions were NRL, The Boeing Company, Lehigh University, and Carnegie-Mellon University, to which was added Georgia Institute of Technology because of special capabilities in surface physics.

Two other universities had supplementary roles for special purposes: At a time when graduate students specializing in the electrochemistry of corrosion were almost

nil, both in the program and nationally, such students became enrolled at American University under well-qualified thesis supervision; hence, American University became a supplementary member of the program to ensure the involvement of at least a few electrochemistry graduate students, in this case studying the role of anions in corrosion reactions. At the University of Florida, Professor M. Pourbaix became available as a visiting professor and consultant to the program, and for this reason the University became a supplementary member, concentrating on experimental methods to apply Pourbaix' potential-pH method for analyzing the corrosion behavior of complex alloys (commencing with chromium steels).

There were no exclusive charters at any of the institutions, but in general the emphasis at Lehigh was on surface chemistry, that at Carnegie-Mellon was on physical metallurgy, and that at Georgia Tech was on surface physics. NRL contributed to both basic and applied research, and Boeing's role was to amplify the capabilities of NRL. Boeing and NRL filled an additional role by providing opportunities for graduate students to observe and/or participate in applied research in the course of their graduate careers.

SCC, which is caused by the conjoint action of a corrodent and a stress which may be constant, represents one of the limiting cases of corrosion fatigue (as R-1), which differs from SCC in that in corrosion fatigue the stress is necessarily fluctuating. For this reason corrosion fatigue in a limited sense was considered an appropriate subject to be included in the program, and particularly appropriate for a DoD program, since corrosion fatigue is said to be the major cause of failures in vehicles and in moving machinery. Analysis shows that there is no such thing as a simple method of generating the general engineering corrosion-fatigue characteristics of a given alloy, however, and accordingly from midprogram onward the corrosion-fatigue studies were restricted to academic research on mechanisms. Research on corrosion-fatigue mechanisms was also conducted at NRL with Navy funds but associated with the program.

The alloy families of interest were titanium, high-strength steels, and aluminum, and the relative emphasis on the three systems was set at 3:2:1. The reason for this relative emphasis was not alone the relative importance of the problem to DoD, but also the relative amount of accumulated knowledge in the three systems and the activity of producers on the problem in the area of their own products.

#### *Modus Operandi*

The program was conducted as a national one in the sense that it was fully integrated into the national technical community. Reports from the program were given unlimited distribution, and attendance at the quarterly meetings (described briefly below) was open to personnel from outside the program, subject only to the limitations of manageability. It was found that keeping the agenda of the quarterly meetings to a single narrow topic (e.g., titanium alloys) accomplished several ends: It permitted an in-depth review of the subject matter, it eased the problem of limiting outside participants, and it promoted interchange between persons working in different disciplines such as surface physics, electrochemistry, metallurgy, crystallography, and mechanics. The program profited immensely by the regular participation of outsiders.

The program was integrated into the national technological community in another manner, namely, by sharing costs. For example, in studies in which, to have technological significance, portions of large heats (batches) of alloys were required, these alloy heats were sometimes procured by other DoD interests, and the small amounts required for SCC studies were traded to the ARPA project in return for the stress-corrosion information generated. Mixed support of another type was practiced in which students whose stipends were paid from one source had the costs of their laboratory supplies and services paid by the ARPA program. These jointly supported activities



provided not only breadth of contact but also economies which in the case of large alloy heats were of important magnitude.

Also as part of the design of the program to serve the national technological community, personnel in the program were encouraged to present the output of their research at various types of technical meetings. The effectiveness of this policy is evident in the Presentations section of the Abstracts of Achievements.

## Documentation

This report is primarily technical, but a brief background account is given here for the interested reader.

As another part of the final reporting sequence, there is in preparation a monograph on the state of the art of stress-corrosion cracking (SCC) of titanium alloys, high-strength steels, and aluminum alloys. That monograph is designed to be not only a summary of what has been contributed to the subject by the ARPA program, but a state-of-the-art summary without restriction as to source of contributions. The monograph will therefore be the most useful technical summary of the program for most purposes, for in it the pertinent output of the program is integrated into the entire literature on the subject.

The present report is limited to contributions from the ARPA program. Such contributions from a program as large and as productive as this one cannot be *detailed* in a manageable fashion in a single document such as the present report, but the key contributions are given herein in a consolidated narrative form. In addition, Abstracts of Achievements, modeled after the Interdisciplinary Laboratory reports, are given, together with references to the literature, so that the reader has a key directly to the technical literature of interest to him. The present report was written at the end of the program, and by the nature of the publication machinery of the technical societies many of the manuscripts generated by the program have not yet been printed. In such cases the journal or society is noted so that the interested reader can monitor the appropriate literature for the appearance of a paper of special interest. Requests for reprints should be directed to the individual authors. Qualified recipients may request from the Defense Documentation Center those reports for which accession numbers are given.

In the present report the author uses the term *stress-corrosion cracking* (SCC) to designate a cracking process caused by the conjoint action of a stress (which need not be fluctuating), and a corrodent. The term *corrosion fatigue* is used to designate a cracking process caused by the conjoint action of a fluctuating stress and a corrodent. The terms are thus based upon macrophenomenology rather than mechanisms, and the introduction of new terms such as *corrosion-assisted crack growth* and *subcritical cracking* becomes unnecessary.

The emphasis on reporting was to get contributions presented expeditiously at standard technical society meetings and published expeditiously in their journals, and the function of the quarterly reports was most importantly to notice the writing and the publication of such manuscripts in the standard literature.

## THE PROBLEM OF THE MACROSCOPIC TEST

Regardless of how small the scale of events which may cause SCC, ultimately it is the macroscopic phenomenon which must be controlled. The traditional method for

characterizing SCC was to stress a specimen in a corrosive environment and report time to failure, usually meaning time for complete separation of the specimen. Although this parameter has afforded progress, particularly in the low-strength alloys, it is a defective parameter because it represents the undifferentiated *sum* of the effects of three processes, (a) incubation (usually film breakdown plus corrosion pitting), (b) SCC, and (c) terminal mechanical overload fracturing (Fig. 2). If an alloy is not susceptible to pitting, then a (smooth) specimen may give an indication of an infinite time to failure, i.e., the alloy may appear to be immune to SCC, whereas in fact it may be highly susceptible to stress-corrosion crack *propagation*. (Titanium alloys in water exemplify this behavior.) Alloys with different fracture toughness characteristics require different lengths of stress-corrosion cracks (and hence different exposure times) before the onset of overload fracturing; thus time-to-failure data could lead to grossly erroneous inferences regarding the relative SCC characteristics of these alloys. Some materials are so brittle that if they are stressed and a corrosion pit forms, the pit can initiate "brittle fracture," and an indication of high susceptibility to SCC might be inferred from a test in which in fact no SCC has occurred at all. (The 5% Cr die steel heat treated to maximum strength tends to behave in that fashion.)

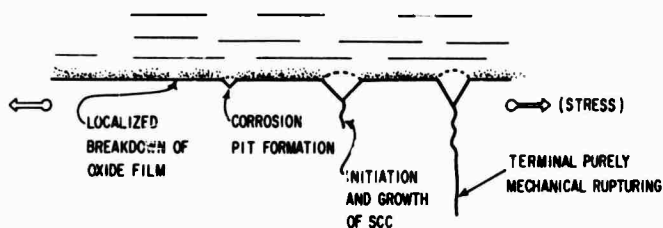


Fig. 2 - Sequence of events (left to right) by which a metal under stress with an originally smooth surface undergoes successively localized film breakdown, corrosion pitting, stress-corrosion cracking, and finally mechanical rupture

The foregoing complications are illustrated in Fig. 3, which is a plot of depth of pitting plus SCC plus mechanical fracturing on the ordinate vs time on the abscissa.

At the beginning of the program, the great bulk of data in the literature and most of that being inserted into the literature were of the undifferentiated time-to-failure type, and as has been shown above, this sort of data can be very misleading about stress-corrosion characteristics. One of the tasks of the program, therefore, was to establish the true SCC characteristics of the structural alloys of most current importance to military designers.

To do this characterization, as well as to conduct other studies both basic and applied, one or more specimen types were used containing pre-existing cracks. This tactic has three advantages: (a) It obviates waiting for a corrosion pit to grow, saving time. (b) It enables one to avoid an erroneous conclusion of immunity to SCC because of a nonpitting combination of alloy and environment. (c) It enables one to get a conservative evaluation by evaluating the material in the presence of the ultimate flaw, namely a sharp crack. There is a fourth advantage, for if the specimen meets certain criteria, the methods of fracture mechanics can be used to predict from the behavior observed in one geometry of specimen and crack what will happen in other geometries.

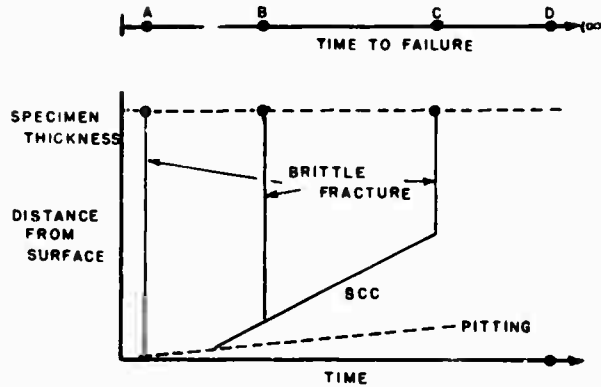


Fig. 3 - The time-to-failure information from stress-corrosion cracking tests of smooth specimens, as plotted in the line at the top, indicates an ascending order of merit with respect to stress-corrosion cracking from A through B and C to D. In point of fact, as shown schematically in the lower portion of the figure, B and C may have the same SCC characteristics but different fracture toughnesses. The SCC characteristics of A and D have not really been measured at all.

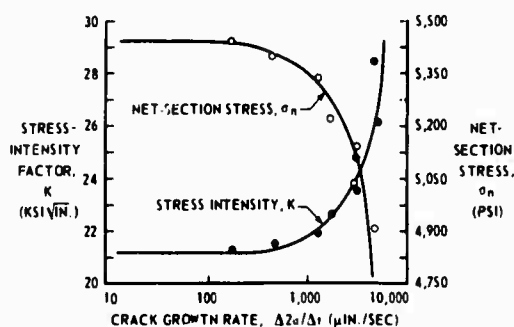
Fortunately for the program, the high level of activity in the fracture mechanics field during the decade preceding the program had produced technological information on various specimen geometries which become useful to the problem of SCC, as will be noted later in this report.

## HIGHLIGHTS OF PROGRAM ACHIEVEMENTS

### Specimens and Macroscopic Test Methods

During the course of the program the methods of fracture mechanics were demonstrated to afford predictability of stress-corrosion behavior from one geometry of specimen and stress configuration to another, whereas nominal stress was shown to be misleading (Fig. 4). The stress-intensity factor  $K$  thus was shown to be the most useful

Fig. 4 - Stress-corrosion cracking data for Ti-8Al-1Mo-1V in salt water. Specimen is stressed at the crack line and the crack growth rate is measured. (Chronologically the experiment proceeds from right to left in this figure.) Experiment shows that as  $K$  decreases (because of crack growth), the crack growth rate decreases, but meanwhile the nominal stress (net section stress) increases. This is an illustration of the inability of net section stress to correlate with cracking behavior. Extrapolation of data indicates a  $K_{ISCC}$  of about  $21 \text{ ksi}\sqrt{\text{in.}}$ .



way to quantify stress in the presence of a stress-corrosion crack. Evidence was found that for titanium alloys there is a threshold value of  $K$  below which SCC is not expected (for a given combination of alloy and corrodent), and this threshold was designated  $K_{Iscc}$ . In the absence of positive knowledge that a true threshold exists, an arbitrarily defined  $K_{Iscc}$  (such as "nil crack growth in 1,000 hours") does indeed convey more information than an index of the patience of the experimenter or his skill with instrumentation; for at slightly higher  $K$  levels, one can make the positive statement that SCC will occur.

To fully characterize the SCC of a given alloy in a given corrodent, one would like to have cracking kinetics as a function of  $K$  all the way from a threshold ( $K_{Iscc}$ ) if one exists to  $K_{Ic}$ , the stress intensity at which brittle fracture occurs. Even if one has only the value  $K_{Iscc}$ , and even though in a given system this may not be known to be a true threshold but may represent, for example, the minimum  $K$  at which SCC is observed in 1,000 hours, the  $K_{Iscc}$  numbers can be plotted as a function of yield strength to produce an interesting analysis of the relative merits of various compositions or heat treatments in a given alloy family. In such a plot (Fig. 5), one can simplify the Irwin equation for a surface crack by assuming yield-strength stresses, and assuming that any surface flaw will be long compared with its depth and will lie perpendicular to the stress field, he can then draw a series of straight lines as shown in Fig. 5. Any one of these represents conditions for a given flaw depth, and the line simply means that if one may have a given flaw size as represented by the line, he must have a material with a  $K_{Iscc}$  lying above that line to avoid SCC.

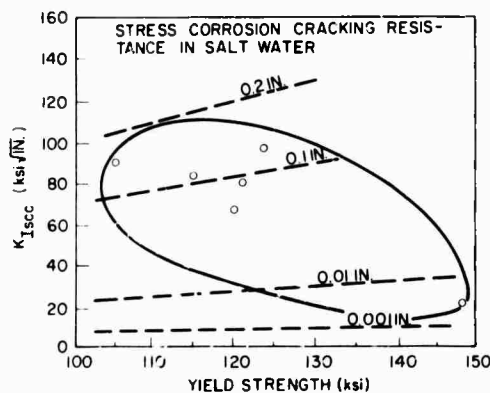


Fig. 5 -  $K_{Iscc}$  data in salt water for six commercial heats of Ti-6Al-4V rolled to plates 1-in. thick. All  $K_{Iscc}$  data for commercial heats of this alloy have been found to lie within the oval. The broken lines indicate  $K_{Iscc}$  values which an alloy must have (or exceed) in order to avoid SCC initiating at a long flaw of the depth shown on the line, assuming yield stresses. (Data show that no commercial alloy can tolerate a flaw as deep as 0.2 in. if the operative stress equals the yield strength.) The ordinate is linearly proportional to load-carrying capacity in the presence of a standard flaw.

$K_{Iscc}$  can be determined by a number of specimens, some set at  $K$  levels above and others below the  $K_{Iscc}$  level. The program showed that there are alternative ways to determine a threshold. For example, one can use the "wedge-loaded" (crack-line-loaded) sheet tensile specimen and await arrest of the stress-corrosion crack, or one can use a load-relaxing system such as an elastic ring to stress a specimen which experiences relaxation as the stress-corrosion crack advances (Fig. 6). It was shown elsewhere during the program that a specimen similar to the one of Fig. 6 can be self-stressed with a bolt and used as a stress-corrosion specimen. During the program the specimen of Fig. 6, self-stressed with a bolt instead of the elastic ring, has been shown to be extremely useful for characterizing the SCC behavior of high-strength aluminum alloys by determining the rate of crack growth as a function of  $K$  (Figs. 7, 8). Such a test has been found far more rapid and more discriminating than the traditional methods.

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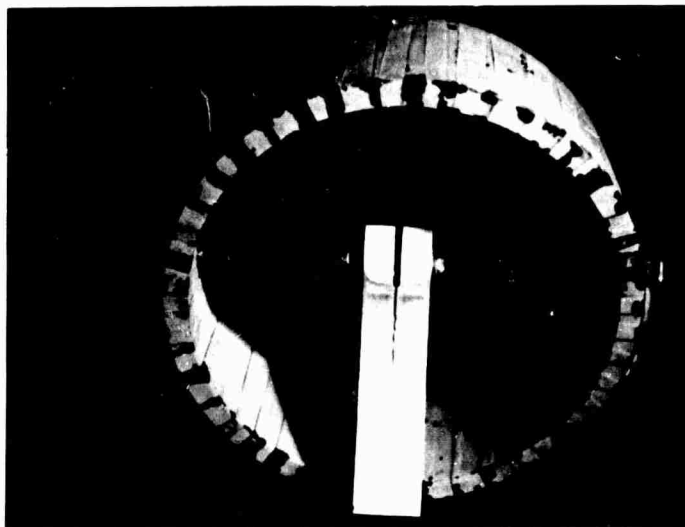


Fig. 6 - DCB aluminum alloy specimen ( $1 \times 1 \times 3.5$  in.) stressed by an elastic ring which relaxes as the crack propagates. (Ring is made of high-strength steel wrapped with tape to prevent stress-corrosion cracking.) Load on ring is monitored by strain gage (not shown).

Since  $K$  has been shown to be the proper way to quantify stress around a stress-corrosion crack, and since SCC kinetics have been found to be  $K$ -dependent, specimens having the property of constant- $K$  conditions regardless of crack length would be of obvious interest. Two such constant- $K$  specimens were studied in the program. One of these, designated the tapered, double-cantilever beam (DCB) specimen, has given experimenters problems with the arms breaking off, and that was found to be true using the specimen for SCC, even though the experimenters were expert with that particular specimen. It was found possible, however, in using this specimen at a number of  $K$  levels, to extrapolate the crack rate to zero, which was found to correspond to  $K_{I_{SCC}}$  for the same steel as determined by a beam specimen. The other constant- $K$  specimen, sometimes designated the double-torsion specimen and sometimes the Outwater specimen (after its inventor), is of additional interest because of its simplicity—it can be satisfactorily prepared from a sheet of metal using a bandsaw. For constant- $K$  conditions the specimen can be satisfactorily stressed by a dead-weight-lever system, and it appears to be well behaved in stress-corrosion tests, at least for high-strength steel.

A small inexpensive self-stressed specimen was developed for possible use as a quality-control specimen for sheet materials.

The newcomer seeing all the various specimens for measuring SCC characteristics might reasonably ask which one he ought to use. It might be helpful to the metallurgist or engineer to regard this selection question somewhat like the question of which *hardness* test one should use. In both cases the answer to the question depends partly on the geometry of the material of interest and partly on the answer one ultimately gets.

#### Titanium

The resistance to SCC of all the commercial titanium alloys and many developmental and research alloys has been determined using precracked specimens. Electrochemical

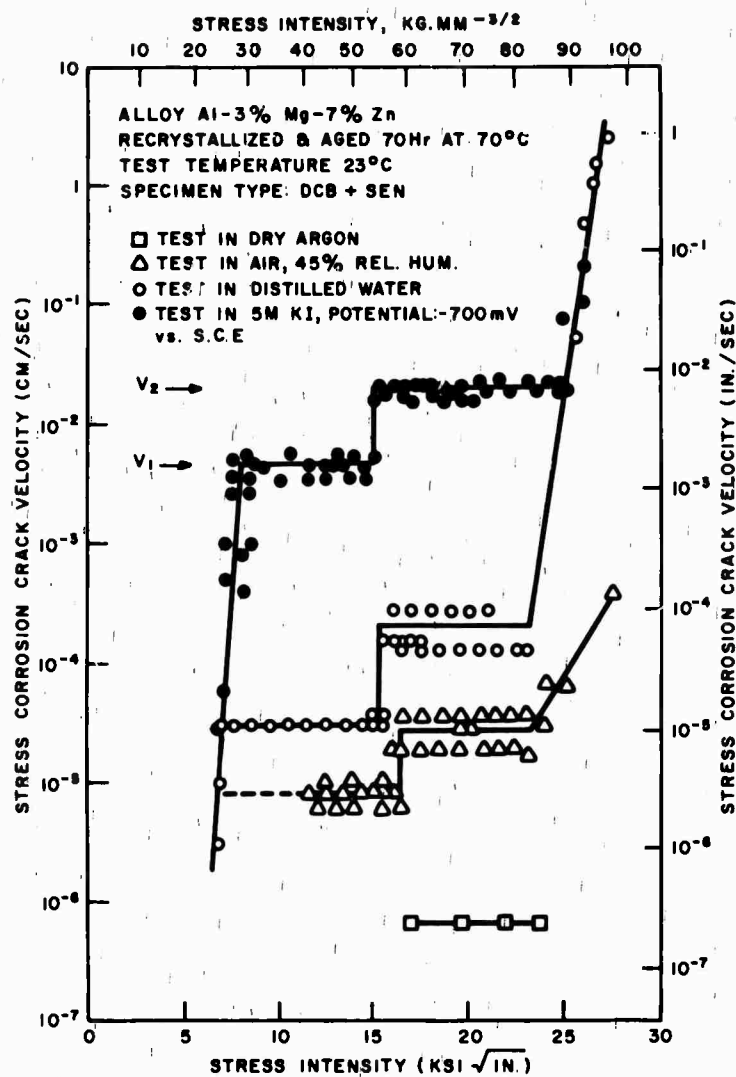


Fig. 7 - Crack-growth rate as a function of K for an aluminum alloy in several environments, illustrating the three stages of the V-K behavior

evidence was interpreted to indicate that for titanium alloys in salt water there is a genuine stress-intensity threshold below which stress-corrosion cracks do not propagate.

The resistance to SCC was found to be strongly dependent upon microstructure and dislocation substructure (Fig. 9). Alpha and alpha-beta alloys that exhibited planar slip in the alpha phase had low resistance to SCC. Beta grains in alpha-beta alloys tended to act as obstructions to the SCC fractures in the alpha phase, but with complications noted below (Fig. 10).

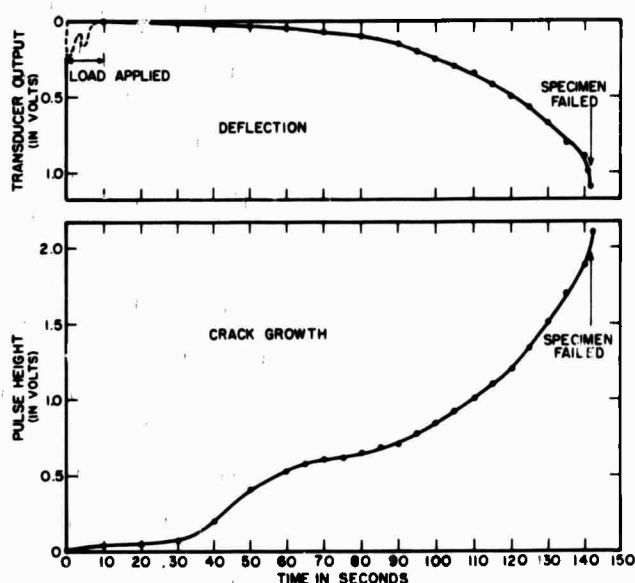


Fig. 8 - Crack-growth rate measurement continues to challenge the experimentalist. An alternative to the clip-gage technique is to monitor the reflection from an ultrasonic pulse (data shown above for a dead-weight-loaded, cantilever-bend specimen of titanium alloy).

Planar slip was found to be characteristic of alloys containing

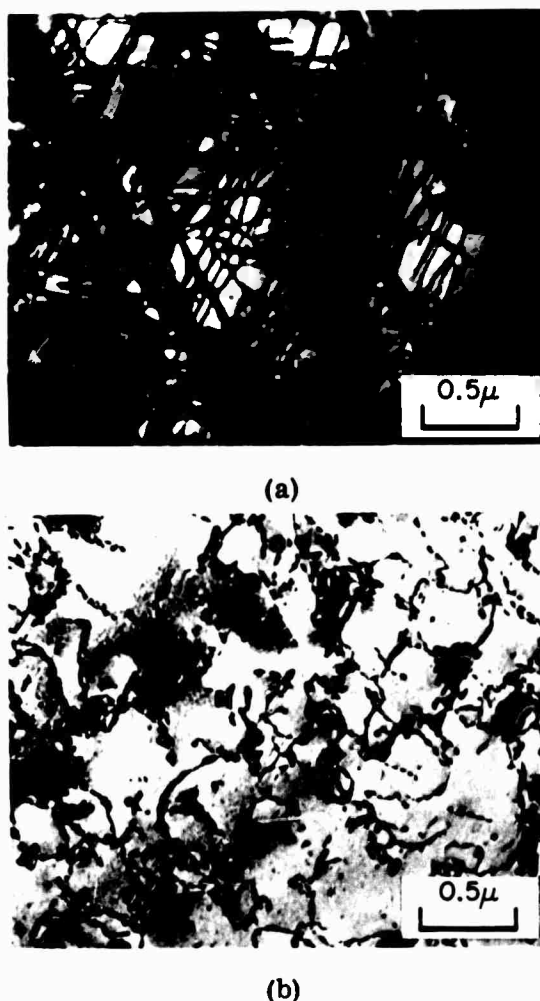
- High oxygen, or
- Aluminum in excess of about 6%, or
- Aluminum in excess of about 5% and tin content of 2.5% or more.

The formation of ordered domains of  $Ti_3Al$  or  $Ti_3(Al, Sn)$  in the alpha phase further restricted slip and decreased SCC resistance.

In an alpha-beta alloy, increasing the proportion of beta by increasing the amount of alloying elements such as Mo or V increased SCC resistance, perhaps by the crack-obstructing mechanism mentioned above (Fig. 11). But decomposition of the beta phase (to form omega,  $Ti_2Cu$ , or  $Ti_5Si_3$ ) may embrittle the alloy and markedly lower its SCC resistance.

Of the common commercial alloys, Ti-8Al-1Mo-1V was found to be the least resistant to SCC, Ti-4Al-3Mo-1V was found to be highly resistant, and Ti-6Al-4V was found to have intermediate resistance. These observations were again observed to be correlative to the type of dislocation substructure.

In the all-beta alloy Ti-13V-11Cr-3Al, SCC fractures were observed to occur on or near the (001) plane. The crystallography of twinning of another all-beta alloy (Ti-11.5Mo-6Zr-5Sn) was found to be different from that of most other bcc metals. Mechanical fracture occurs macroscopically parallel to (001), but microscopically the fracture mechanism is not cleavage but microvoid coalescence. Unfortunately, aging this alloy to optimum strength (153 ksi yield) and toughness ( $K_{Ic} = 66 \text{ ksi} \sqrt{\text{in.}}$ ) produced minimum resistance to SCC in halide solutions. The SCC fracture path in this alloy is intercrystalline, in contrast to the transcrystalline fracture path seen in most titanium



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Fig. 9 - Coplanar dislocation arrays (above, associated with SCC-prone titanium alloys) and tangled dislocations (below, associated with SCC-resistant alloys)

alloys. The formation of omega phase during aging was observed to be an important factor reducing the ductility of the aged alloy; this phase is distributed as small particles (100 to 1,000 Å), but even so may constitute a high volume fraction of the alloy.

The SCC fractures in the alpha phase of alloys lie  $15^\circ \pm 2^\circ$  from the basal plane of the hexagonal lattice. This relatively good consistency in crystallographic habit plane has led the resulting flat fracture facets to be termed cleavage (Figs. 12 & 13). The entire SCC fracture surface, however, is not cleavage, but cleavage areas are interspersed with rupture dimples (microvoids) which resemble the dimples of a purely mechanical fracture (Fig. 14). Thus, a stress-corrosion crack appears to be formed by two mechanisms, one (cleavage) involving stress plus an environmental reaction, and the other (dimples) wholly or largely of mechanical origin. The proportion of the dimple areas increases as  $K$  increases from  $K_{I_{SCC}}$  to  $K_{I_C}$ , at which stress intensity the remaining ligament separates entirely by dimple rupture.

Methanol and several other organic fluid environments, including hydrocarbons, were observed to cause the SCC of titanium alloys. Carbon tetrachloride also caused



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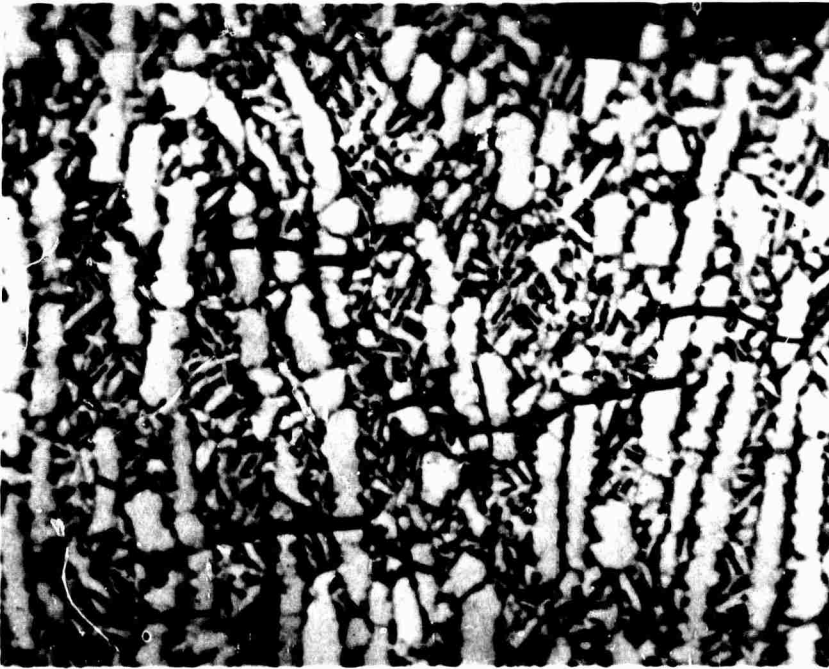
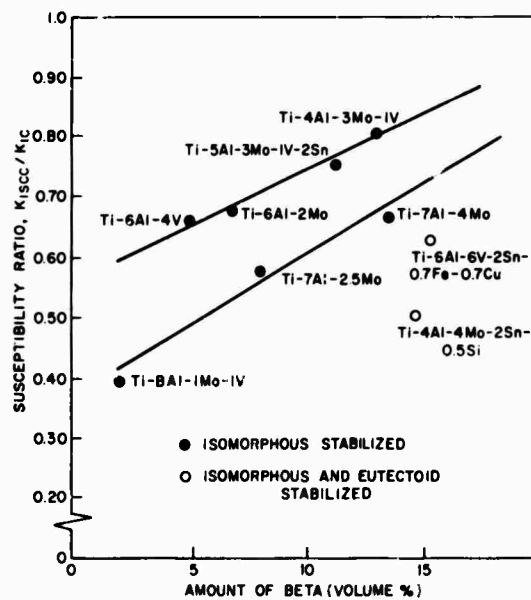


Fig. 10 - Partial stress-corrosion cracks in alpha-beta titanium alloy showing cracks in the alpha phase arrested by the beta phase, 1,000X magnification.

Fig. 11 - Increasing proportion of beta in alpha-beta titanium alloys tends to increase the ratio  $K_{Isc}/K_{Ic}$



severe cracking. These findings have practical implications in the selection of paints and of cleaning and degreasing fluids. Except for liquid metals, carbon tetrachloride is the only environment not containing hydrogen (assuming the  $CCl_4$  was free from  $HCl$ ), which cracks titanium.



NOT REPRODUCIBLE

Fig. 12 - Fractograph showing cleavage surface typical of stress-corrosion cracking in titanium alloys in water at a low K level. 6,000X magnification.

Slow crack propagation was observed in titanium alloys in the absence of atmospheric moisture and also in a hard vacuum somewhat better than  $10^{-7}$  torr. In these specimens as in those cracked in organics and in aqueous liquids, the fracture was cleavage interspersed with dimples. Heat treatment which reduced the hydrogen content of the titanium reduced its tendency to slow crack growth in vacuum (Fig. 15).

Methods were developed and applied to elucidate the nature of the corrodent near the advancing crack tip. With neutral salt water as the corrodent, the pH at the advancing crack tip was highly acid (about 1.6). The pH and the potential place the crack tip in a thermodynamic regime in which the hydride may be stable, but not an equilibrium oxide. The addition of  $\text{FeCl}_3$  to the salt water increased the SCC resistance of the titanium, perhaps by substituting the reduction of copper for the reduction of hydrogen as the cathodic reaction.

One model which has been proposed for SCC of titanium, in accord with the observations noted above, is the hydrogen model. The reaction of a clean titanium surface with any of the hydrogen-bearing environments studied would release hydrogen which would be expected to react with or dissolve in the titanium. In aqueous salt solutions, the pH at the growing crack tip remains sufficiently acid (because of the occluding action of the SCC path) that repassivation is not possible at the crack tip, which continuously provides clean surfaces for reaction to remove more hydrogen from the corrodent. Thus the function of the precrack in specimens tested in salt water is to provide a little local straining plus the restriction to diffusion which will permit the acidity to remain high locally, whereas smooth specimens tested in salt water would repassivate because of the inability of the geometry to keep the acidity high locally. In methanol, however, the situation is different because the product of the reaction of titanium and methanol is soluble in methanol, i.e., the reaction product does not form a protective film in the

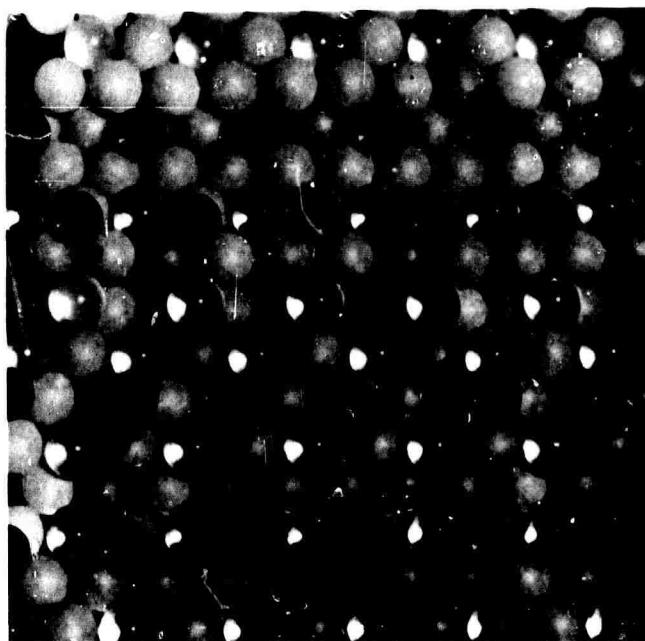


Fig. 13 - Ball model of simulated SCC fracture surface in Ti-Al alloy. Aluminum atoms on base surface are designated by clear balls and on the matching plane by dark balls. The fracture plane occurs where there is the highest concentration of Ti-Al bonds in ordered alpha.

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*bulk* environment. This has been concluded to be the reason *smooth* specimens will initiate SCC in methanol.

Straining Ti-Al alloys in salt water was observed to cause large increases of the active range during anodic polarization, and this too is consistent with the picture of reactions occurring near the crack tip. A computer program has been developed for solving the complex electrochemical transport equations involved in SCC. The aspect ratio was found to dominate all else.

Ti-Al alloys were found to show the same precipitation of hydride at coplanar dislocations in SCC specimens as in slow strain-rate hydrogen-embrittlement specimens, again suggesting the hydrogen model.

Acceptance of the hydrogen model would require a resolution of two apparent anomalies: a) the observation of SCC in reasonably pure  $\text{CCl}_4$  (containing traces of water), and b) the observation that increasing  $[\text{Cl}^-]$  increases SCC crack-growth rates at a given K level.

## Steels

The SCC characteristics of a large number of commercial and near-commercial steels were determined using salt water and natural seawater (Fig. 16). The use of pre-cracked specimens to determine SCC characteristics of alloy steels in seawater can save half a year to a year, which otherwise may be required to generate the pits which in turn initiate SCC. (A precracked specimen may, however, give erroneous data if it is



Fig. 14 - Fractograph showing flat cleavage areas plus dimpled (mechanical rupture) areas typical of SCC in titanium alloys in water at a  $K$  level much higher than that of Fig. 12

stressed to a high level before being placed in an SCC test at a lower stress level.) From the data of Fig. 16 it is apparent that the maraging steels and at least some of the precipitation-hardening steels were clearly superior to the conventional martensitic steels at the same strength level.

The following observations were made on low-alloy martensitic steels: Silicon content had no effect on  $K_{Isc}$ , but above about 1.5% the increased silicon greatly retarded the cracking kinetics at a given  $K$  level. Reducing the grain size also decreased the cracking kinetics, but did not affect  $K_{Isc}$ . Increasing the manganese or carbon content caused markedly reduced  $K_{Isc}$  values (Figs. 17, 18). None of the following metallic alloying elements was observed to have a significant effect on  $K_{Isc}$ : nickel, cobalt, chromium, and molybdenum.

Fig. 15 - Effect of hydrogen content (varied by vacuum treatment) on fracturing of a commercial titanium alloy in various modes. The line designated  $K_{IH}$  represents the stress intensity above which a crack propagates in an inert environment, presumably due to internal hydrogen.

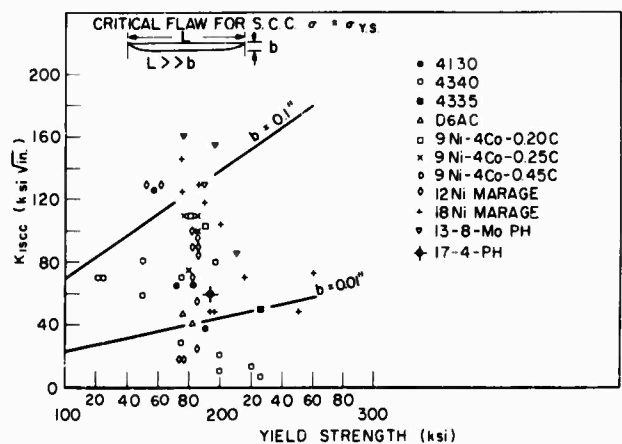
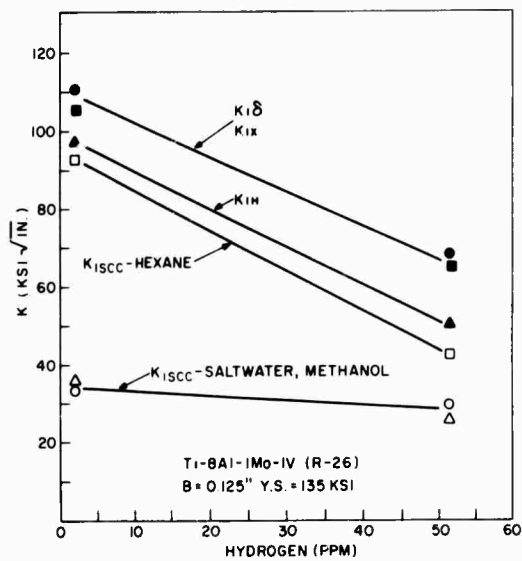


Fig. 16 -  $K_{ISCC}$  data in salt water for a number of commercial alloy steels made in production-size heats. The strength range covers strengths of interest to deep-diving submersibles, rockets, and manned aircraft. Flaws of the depth shown in a given steel would propagate stress-corrosion cracks at yield-strength stress unless the  $K_{ISCC}$  of that steel lies above the line. The ordinate is linearly proportional to load-carrying capacity in the presence of a standard flaw.

The purity of maraging steels with respect to sulfur and phosphorus was not found to have an important effect on SCC characteristics. The same was observed in low-alloy martensitic steels of the 4340 type.

Among the maraging steels, thermal history appears to have an effect above and beyond its effect on strength. Underaging the 350-grade maraging steel was found to be bad for SCC, whereas overaging was helpful. Overaging of 18%-Ni maraging steel

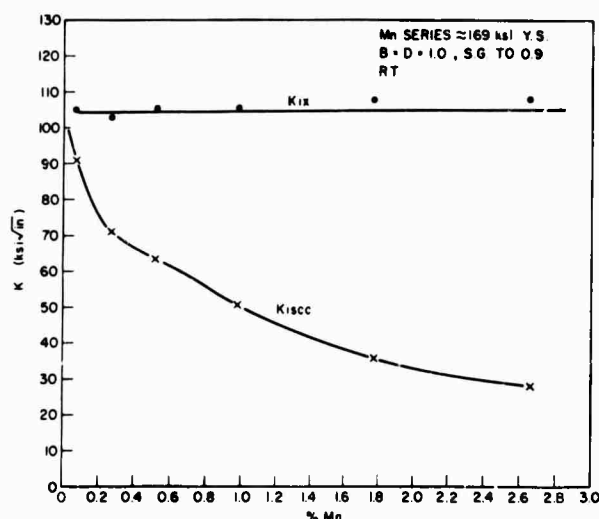


Fig. 17 - Effect of manganese content on  $K_{Isc}$  and on toughness ( $K_{Ix}$ ) of martensitic steel in salt water

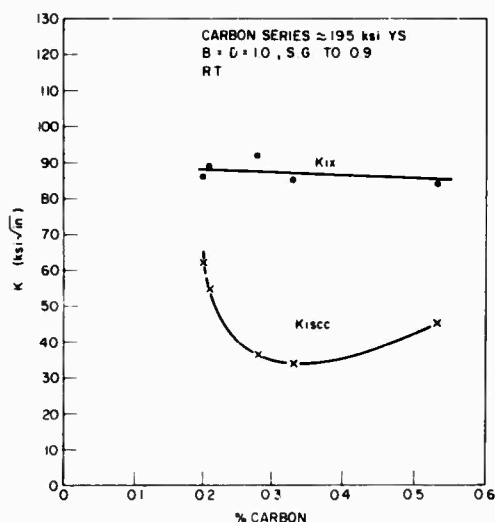


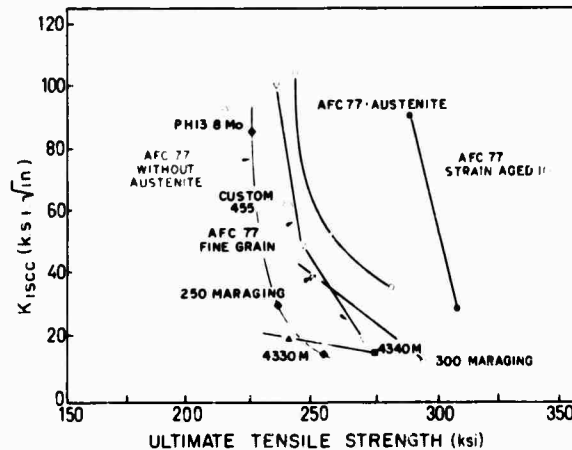
Fig. 18 - Effect of carbon content on  $K_{Isc}$  and on toughness ( $K_{Ix}$ ) of martensitic steel in salt water

produces reverted austenite, the primary site for which appears to be the compound  $Ni_3 Mo$ .

$K_{Isc}$  has a complex curvilinear dependence on strength level, but for a given martensitic steel in the 175- to 185-ksi yield-strength range, a 7% increase in yield strength (by differences in tempering treatment) caused a 20% loss in  $K_{Isc}$ , which is linearly proportional to the load-carrying capability of a component containing a standard flaw. The program demonstrated, however, that strengthening by strain aging (in a precipitation-hardening steel) entails a smaller penalty in SCC than the strengthening of martensitic steel by choosing the tempering temperatures, thus providing a possibly useful avenue for further advances for special needs (Fig. 19).

Stress-corrosion cracks are commonly thought to be characteristically multiply branched, because SCC was first observed in cold-worked products, which have complex

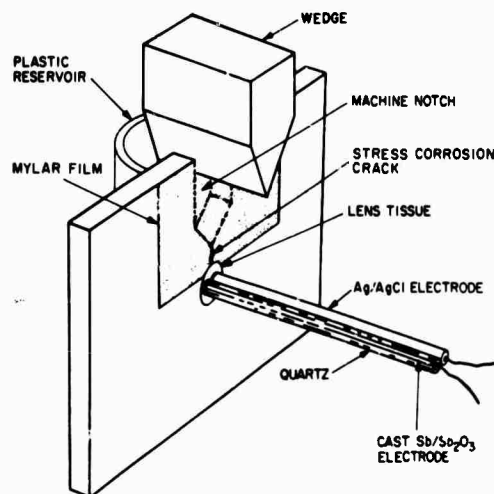
Fig. 19 -  $K_{Isc}$  for several commercial steels and one developmental steel (AFC 77) in salt water. Note, for AFC 77 in any given condition, the rapid decrease in  $K_{Isc}$  with rising ultimate tensile strength. Note also that by increasing the strength by strain aging, the strength can be increased over that of regular AFC 77 by more than 50 ksi while maintaining the same  $K_{Isc}$ .



residual stress patterns that change continuously as the article cracks. In the present program it has been found with many materials that the crack-growth rate rises sharply with increasing  $K$  until a point ( $K_{In}$ ) of apparent process saturation is reached, beyond which the rate is more or less independent of  $K$ . If the material is reasonably isotropic, then at a  $K$  level of about  $2K_{In}$  the crack will tend to divide or branch. This finding is useful in understanding tests in which the crack divides and thereby terminates the utility of the experiment.

During the course of the program, methods were developed which for the first time were successful in measuring the pH near the tips of growing stress-corrosion cracks in steel (Fig. 20). These methods employed successively color-change pH indicators,

Fig. 20 - One method for determining the pH at the tip of a stress-corrosion crack. The potential and pH probes rest against a small paper disk (thin to minimize the solution required to moisten it), and are connected to high-resistance recorders. They do not register a reading until the crack propagates to the disk and moistens it. (The disk does not contain solutes which affect pH.) A glass electrode designed for surface measurements can be used in place of the antimony oxide electrode.



the antimony electrode, and finally the glass electrode, and all three methods gave the same result. This work on crack-tip chemistry gave new insight on SCC (and eventually on most forms of localized corrosion, as will be discussed in a later section). It was found that regardless of the pH of the bulk solution (external to the crack) or the potential impressed upon the steel, the combination of potential and pH at the crack tip are such as to be favorable for the reduction of hydrogen (Fig. 21). This finding makes it unnecessary to postulate any mechanism for SCC in (high-strength) steel other than that commonly termed *hydrogen embrittlement*. The mechanism of hydrogen embrittlement has

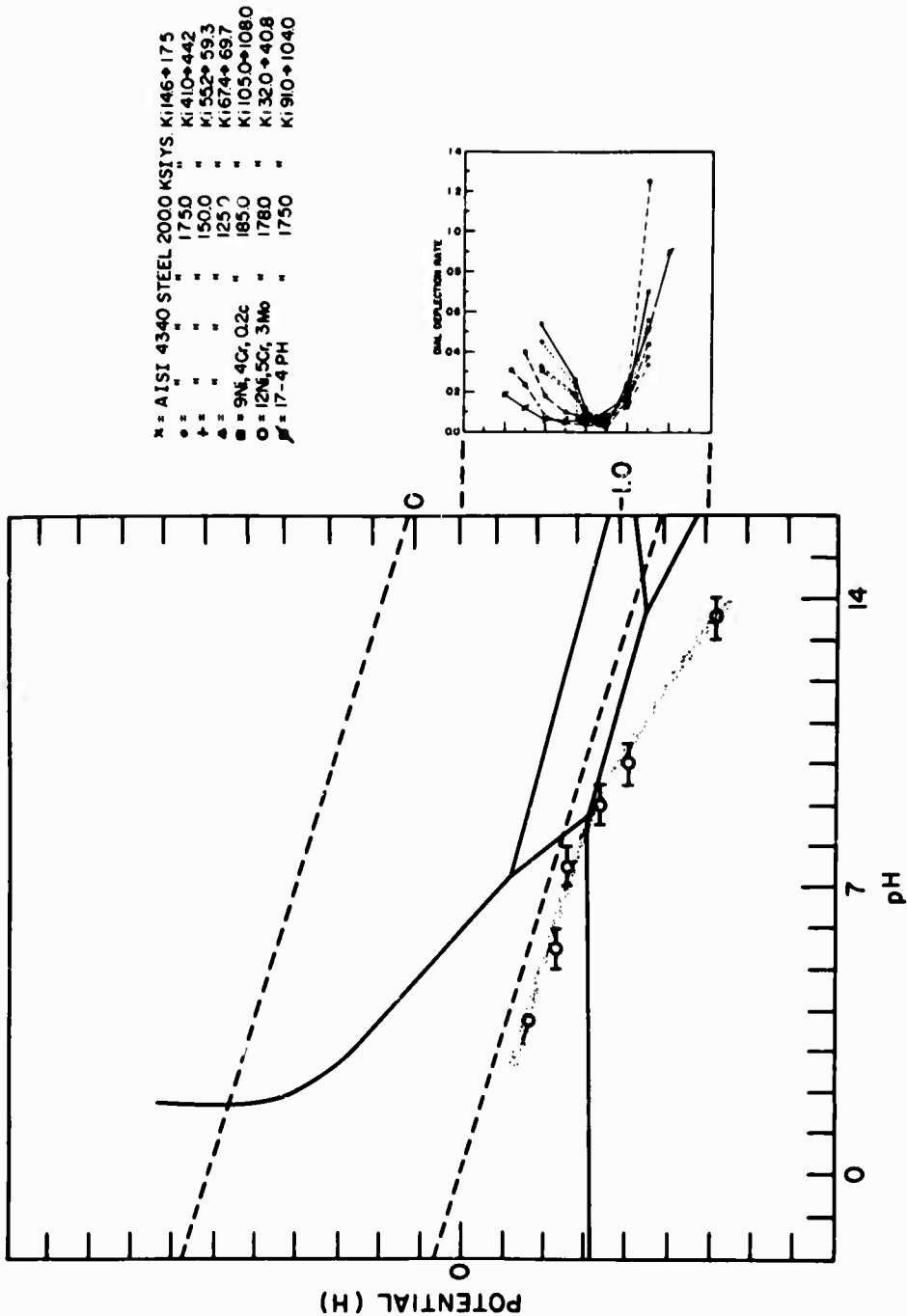


Fig. 21 - pH at the tips of growing cracks in neutral 3.5% NaCl solution, specimens potentiostatted to various levels. Curves at right indicate a function of crack-growth rate (dial deflection rate) at approximately constant K for a given steel (but different K's for different steels). These data were taken by color-change pH indicator technique but have since been confirmed by the glass electrode. Stress-corrosion cracking in steels occurs only under conditions of local pH and potential which place the crack tip under the hydrogen reduction line (lower sloping broken line).



been postulated to involve the formation of an iron hydride, thought to have been prepared and partially characterized, but work during the program has shown that the alleged iron hydride (prepared by a Grignard method) was really an organic compound of iron.

The work on crack-tip chemistry forms the basis for postulating a new role for either a corrosion pit or a pre-existing crack in initiating SCC: Formerly the pit and crack were viewed as stress concentrators, but it is now concluded that their *essential* role is to produce the local acidity which helps establish the conditions for hydrogen reduction. In the corrosion pit the acidity caused by hydrolytic reactions is retained locally by the porous cap of corrosion products, and in the stress-corrosion crack the local acidity is retained because of the long narrow diffusion path between the crack tip and the external corrodent. These observations are consistent with current findings in the program on the nature of pitting of Fe-Cr alloys (Fig. 22).

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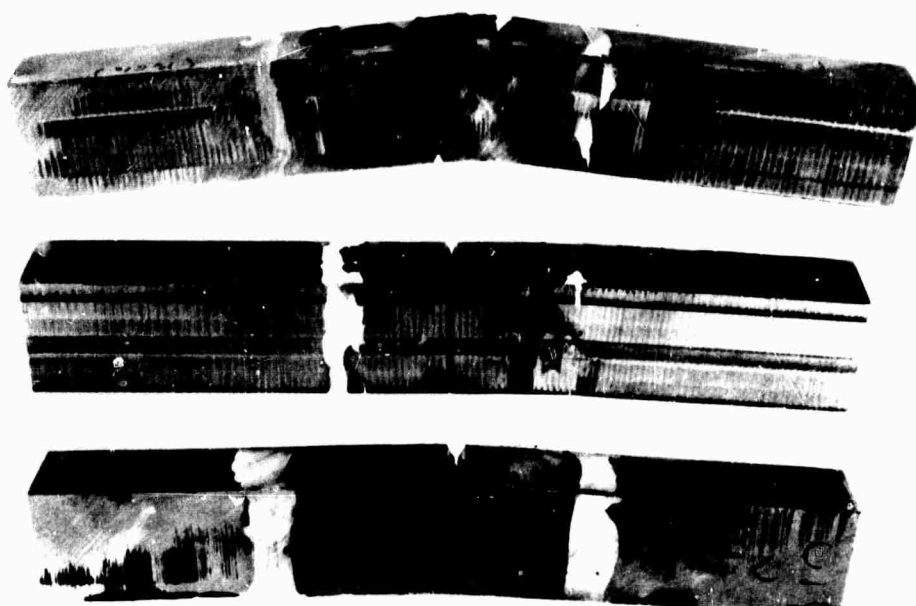


Fig. 22 - Three specimens of a 13-8Mo precipitation-hardening steel whose stress-corrosion cracking characteristics, at first puzzling, become comprehensible in the light of the experiment of Fig. 21. The lower specimen, stressed at a high  $K$ , commenced cracking at the notch. At a lower  $K$  (center specimen) there was no cracking at the notch but, after a delay of 1300 hours, there was rapid cracking under the wall of the corrodent cell. This was attributed to lowering of pH in the crevice under the wall by crevice corrosion so as to cross the hydrogen reduction curve. The upper specimen also cracked immediately at an unnotched area on which a crystal of ferric chloride had been laid to lower the pH locally.

The acidity role of the corrosion pit suggested that inhibitors and buffers which prevent the formation of the corrosion pit would be effective in preventing SCC of a smooth specimen, and this inference was confirmed experimentally. A specimen containing a precrack, however, responds only to a limited degree to inhibitors and buffers:  $K_{I_{SCC}}$  cannot be raised to  $K_{I_c}$  by such additives, doubtless because not enough of such additives are present inside the crack at the crack tip to fully control the local pH.

Cathodic protection can readily effect changes in pH deep within growing stress-corrosion cracks (contrary to a commonly held rule of cathodic protection technology to the effect that cathodic protection cannot function deeper down a crack than about eight times the crack opening dimension). [Partly because of the foregoing discrepancy, an NRL study in another program showed that the factor of 8 cited above was too pessimistic by at least a factor of  $10^3$ .] Cathodic protection has not appeared to be a solution to the problem of SCC in high-strength steel because, although the local hydrolytic acidification can be prevented by cathodic polarization, the conditions are still met for hydrogen evolution and cracking does continue to occur. The rate of stress-corrosion crack growth is highly dependent on potential and goes through a minimum at about  $-0.85$  to  $-0.9$  V (SCE) for all alloy steels which have been studied; this minimum in kinetics corresponds approximately to the potential at which iron becomes thermodynamically stable in water, suggesting that the reason for the minimum may be caused by the transfer of the anodic reaction from within the crack (when electropositive to the minimum) to outside the crack (when electronegative to the minimum). As a practical application of this information, one should be able to achieve approximately the minimum in cracking kinetics by plating with cadmium.

If one studies the details on the fracture surfaces using high-resolution replication electron fractography, one finds that regardless of potential, the fracture surface is one of smooth facets (prior austenite grain boundaries) upon which are superimposed plastic tear ridges. The tear ridges increase in number with increasing stress intensity  $K$ , until at  $K_{Ic}$  the fracture is totally tear ridges surrounding craters (purely mechanical microvoid coalescence, or dimple rupture, fracture). This identical nature of fracture details regardless of which side of the potential minimum one is on is consistent with the conclusion that only one model (hydrogen cracking) is required to account for SCC in high-strength steels.

Consistent with the hydrogen model of SCC in steels, the presence of sulfide in the corrodent (which would tend to promote the entry of hydrogen into the steel) has a strikingly adverse effect on SCC.

One can change the oxide film on the exterior of the specimen from one which is conductive ( $\text{Fe}_3\text{O}_4$ ) to one which is poorly conductive ( $\text{MnFe}_2\text{O}_4$ ), but this change does not appear to have any significant effect on SCC behavior.

The crack tip chemistry studies on *steels* in salt water or in ordinary distilled water showed that the corrodent is concentrated with respect to iron. Thus the newly formed crack surfaces do not behave like pure iron in superpure water, in which environment the iron has been shown to be as inert as platinum.

Large changes in pH locally compared with that of the bulk environment are characteristic of the corrodent in stress-corrosion cracks in all alloy families studied (Fig. 23).

One practical *caveat* appears to be provided by the finding that the behavior of pre-cracked specimens of the stainless steel designated 17-4 PH in (nearly neutral) salt water does not correlate with the poor resistance of this alloy to SCC in service. A possible explanation for this apparent discrepancy is that in service, localized hydrolytic reactions (in crevices, for example) may provide such high local acidity as to create a fundamentally different environment, perhaps also contaminated with sulfur compounds, with a different (and lower)  $K_{Isc}$  from that measured in neutral salt water.

#### Aluminum

The work on aluminum alloys in this program, although by design receiving the least emphasis of the three alloy families, became particularly productive in the more

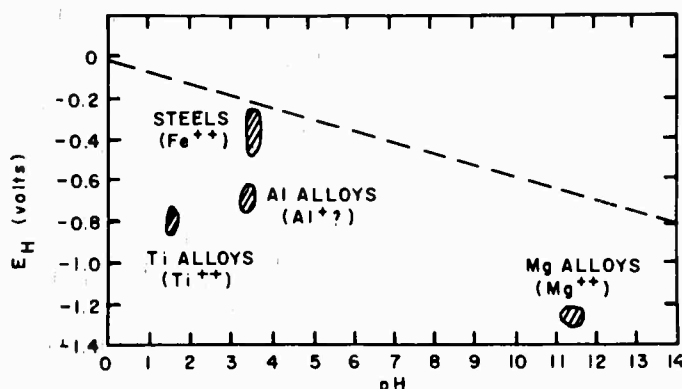


Fig. 23 - Potential and pH data for the tips of growing stress-corrosion cracks in four alloy systems in nearly neutral salt water. Data taken by color-change pH indicator paper technique. Illustrates the large differences between pH of the bulk solution and that at the occluded reaction site. (Hydrogen can be reduced from water below the broken line.)

practical aspects of the problem because of the adoption of the precracked specimen technique (Fig. 24). Wrought products of the Al-Zn-Mg group of alloys which have strengths of special interest to the DoD are highly textured, and SCC is a problem primarily only parallel to this texture. Ordinary bent-beam or tensile specimens cannot be cut in such a fashion as to test this maximum vulnerability direction unless either the plate is very thick or extensions can be welded or otherwise firmly attached to the plate material, which has never been an attractive approach.

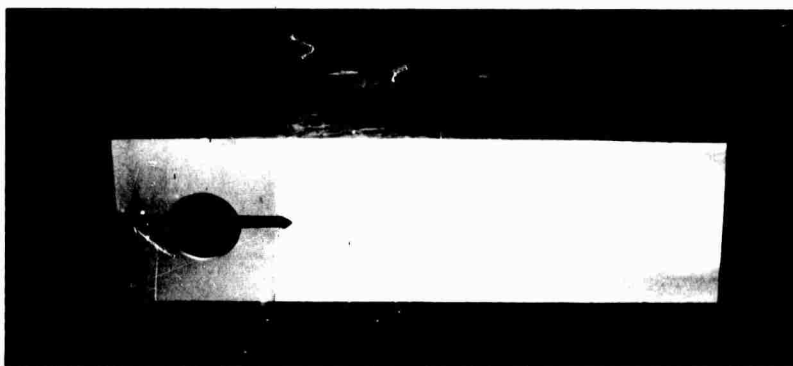


Fig. 24 - Aluminum specimen of Fig. 6 self-stressed (after the method of Novak and Rolfe) by a setscrew. Dark region is paraffin used to insulate the steel set-screw from the crack area. A stress-corrosion crack is seen emanating from the machined notch. This type of specimen was used for most of the characterization data on aluminum alloys in the program.

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Early work with the specimen of Fig. 6 suggested that there was a stress intensity below which SCC stopped, but later work has indicated that, although the rate of crack growth diminishes with decreasing  $K$  at low levels of  $K$ , there does not appear to be any true threshold below which the cracking absolutely stops. Events have shown that the

best way to characterize the SCC behavior of a given alloy is to report the kinetics of crack growth as a function of  $K$ , which will be referred to here as V-K characterization.

A contribution from outside the program has been highly beneficial in using the DCB specimen of Fig. 6. This contribution was the demonstration that one could use a bolt to spread apart the two arms of the DCB specimen to stress it without the need for the proving ring, and that stressing in such fashion still permitted quantification of the stress intensity at the root of the crack. This specimen can then be described as a self-stressed DCB specimen, and it has become a most productive research tool, with demonstrated usefulness for sheet material at least as thin as 0.05 in. Among its other advantages, the self-stressed specimen has that of being suitable for wide distribution for readily assessing, say, the effect on SCC of the environment of an airport runway, or of a deep-diving submersible, or of a noxious chemical.

V-K studies have been completed on a large number of commercial and experimental alloys in various tempers (Fig. 25). These studies have shown that at low values of  $K$ ,  $\log V$  rises rapidly and linearly with increasing  $K$  (Stage I) until a saturation level (Stage II) is reached, after which  $V$  is nearly independent of  $K$ . In some alloys there is a third stage, near  $K_{Ic}$ , in which  $V$  is again dependent upon  $K$ . Curves of  $K \log V$  yield

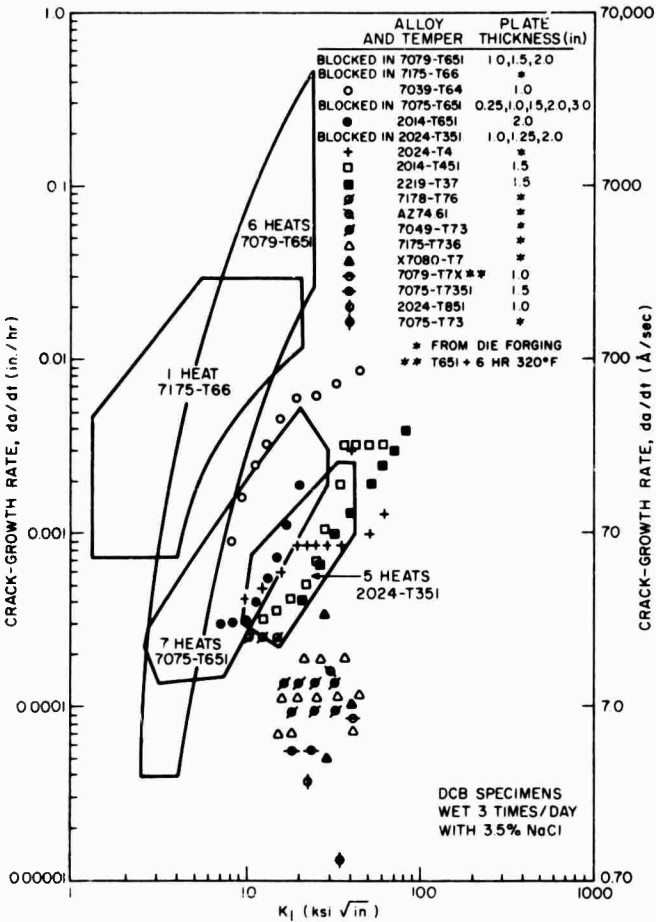


Fig. 25 - Comparison of several commercial and experimental aluminum alloys using the self-stressed DCB specimen and the crack-growth rate method

rangings which agree with established rankings using smooth specimens with two differences: The K-log V rankings are enormously more rapidly obtained, and they are more discriminating than the smooth-specimen rankings when applied to alloys having approximately the same SCC characteristics.

The DCB specimens demonstrated in a very graphic way the magnitude of the effect which quenching stresses can produce in the SCC of aluminum alloys.

The evidence to date is that in Stages I and III the rate of crack growth is little influenced by halide-ion concentration, but the velocity of Stage II apparently can be strongly affected by anion concentration.

Commercial alloys do not experience SCC except when water is present, and only the anions  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  accelerate V (in Stage II) appreciably.

New information was developed on the effects of microstructure on SCC (Fig. 26). It was shown, for example, that the microstructure controlled the cracking process through its effect on the deformation process: Specimens which were strengthened by large Guinier-Preston (G-P) zones exhibited coarse slip characteristics and proved to crack readily, while specimens hardened by small G-P zones exhibited fine slip and cracked slowly. Work on bicrystals revealed that when slip could be transferred across the grain boundary, cracking was slow, but when slip transfer was impeded by the boundary, cracking was rapid.

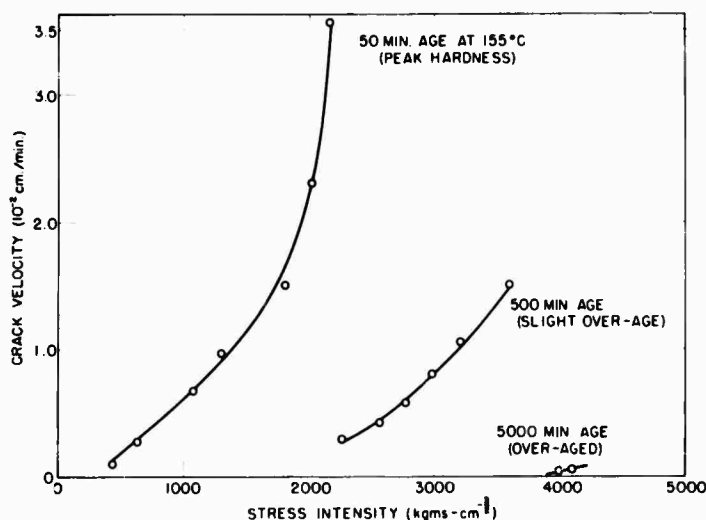


Fig. 26 - Effect of heat treatment on the stress-corrosion cracking kinetics of Al-15%Zn. Transmission electron microscopy shows that the increasing aging time at 155°C causes a progressive decrease in the volume fraction of Guinier-Preston zones.

Neither the presence nor the width of the precipitate-free zone was observed to have any effect on the stress-corrosion susceptibility of a ternary Al-Zn-Mg alloy (Fig. 27). This finding has been explained in terms of slip-band behavior.

Methods have been developed to measure the pH at the tips of growing cracks using both color-change pH indicators and the glass electrode, and in the case of 7000-series

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Fig. 27 - The precipitate-free zone adjoining a grain boundary in an Al-6.8% Zn-2.3% Mg alloy. There has been much controversy over the role that this zone plays in stress-corrosion cracking behavior. Studies on high-purity alloys have led to the conclusion that it is primarily the matrix precipitates, and not the grain boundary precipitate, that determine susceptibility to SCC.

aluminum alloys undergoing cracking from nearly neutral salt water, the pH at the crack tip was found to be 3.2 to 3.5. A macroscopic model was also devised to simulate the sides and the base of a stress-corrosion crack, with the simulated base electrically isolated from the simulated walls. This model has given interesting results to date and gives promise of more to come.

In addition to other basic contributions to aluminum corrosion, two reviews were written by program personnel. One of these was concerned with the aluminum-hydrogen system. A second review treated chemical effects in the corrosion of aluminum and aluminum alloys.

An academic study of the corrosion fatigue of an aluminum alloy demonstrated that hydrogen diffusion is not rate controlling (Fig. 28).

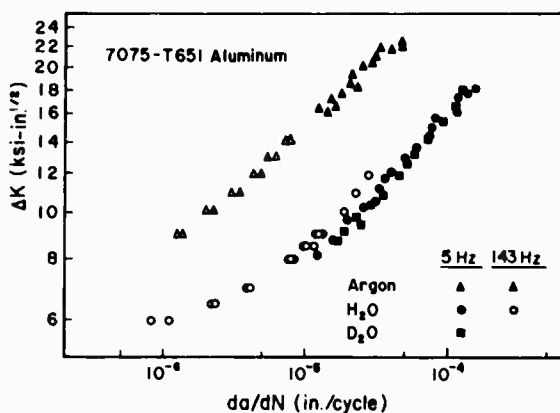


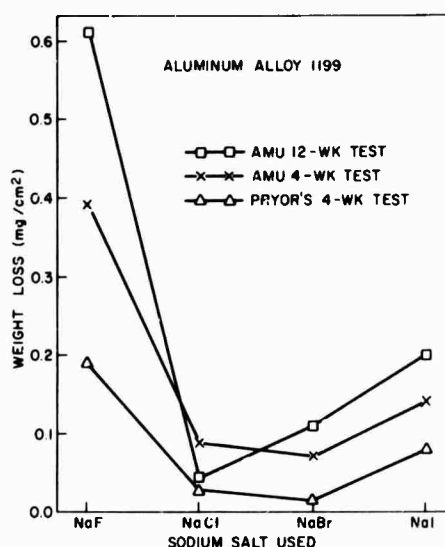
Fig. 28 - Fatigue (in argon) and corrosion fatigue (in water) crack-growth rates in an aluminum alloy. Deuterium studies indicate that hydrogen diffusion is not rate-determining.

## Surface Sciences

Various entries in the Abstracts of Achievements identify contributions of some of the subdisciplines which are sometimes called collectively *surface science*. For example, techniques of Low-Energy Electron Diffraction (LEED) have been advanced by the program to enable the experimenter to study the initial reaction of any chosen gas (however corrosive) with a clean metal surface. An international conference was held in which the status of field ion microscopy and field emission microscopy were reviewed by internationally recognized experts, and the proceedings have now been published. Electron spin resonance studies were made on oxide surfaces exposed to various gaseous species.

As indicated by the foregoing, the program was instrumental in drawing to the attention of surface scientists the existence of a challenging technological problem. As a consequence many basic studies were made using various ones of the newer surface science techniques, much new and interesting information was developed, and more techniques were added to those available to the surface scientist (Figs. 29 to 31). The technique of LEED in particular made significant advances because of the program. The experimental and theoretical difficulties of the program area are such, however, that much more work is required before these newer approaches can make their contributions to corrosion technology.

Fig. 29 - Basic study of the role of the chloride ion in the corrosion of aluminum. Kinetic data show that although there are some quantitative differences between the behavior of the various halide ions, there are no qualitative differences, and the role played by chloride is due to its ubiquity rather than any uniqueness.



The electrochemical techniques and concepts, especially those developed and applied by Evans, Hoar, Pourbaix, and their students, have been shown to be of immediate value both in advancing the theory of stress-corrosion cracking and in guiding technological experimentation. Since electrochemistry is generically a surface science, the tenet that surface science would be useful to the stress-corrosion problem at an early date has thus been vindicated. As one example, it has been postulated elsewhere that hydrogen can only be reduced from aqueous solutions at a cathode, that by making a piece of steel an anode one establishes conditions incompatible with hydrogen reduction and that any SCC occurring under such conditions cannot be attributed to hydrogen. A more sophisticated analysis of the situation is as follows: A given site (electrode) can serve as an anode for the dissolution of iron and at the same time function as a cathode for the reduction of hydrogen, if the potential and pH are favorable.

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Fig. 30 - Field ion micrograph  $\text{Ni}_4\text{Mo}$ . This is one of several modern techniques in surface physics which are useful to study the ultrafine-scale nature of clean metal surfaces.

The experience of the program, in summary, is that there are numerous new areas of surface science capable of yielding important scientific knowledge about metal surfaces and their reaction with environment. The more mature discipline of electrochemistry has been demonstrated to have immediate utility in the understanding of the processes of aqueous corrosion, including stress-corrosion cracking, and in the guidance of future technological advances.

#### ABSTRACTS OF ACHIEVEMENTS

##### Explanatory Notes

These abstracts were prepared by the organization performing the research as a means both of summarizing progress and giving the reader a key to the literature generated by the program. They were modeled after annual reports of Interdisciplinary Laboratories, listing task title, personnel, objective, usually the approach, the achievements, and publications and presentations.

It will be noted that a given task, represented by a single task title, may differ greatly from another in scope, staffing, and productivity. This is due in considerable measure to the broad technical nature of the program and to the fact that each organization grouped its work under a given task title as seemed most effective for conveying the output to the imagined readers.



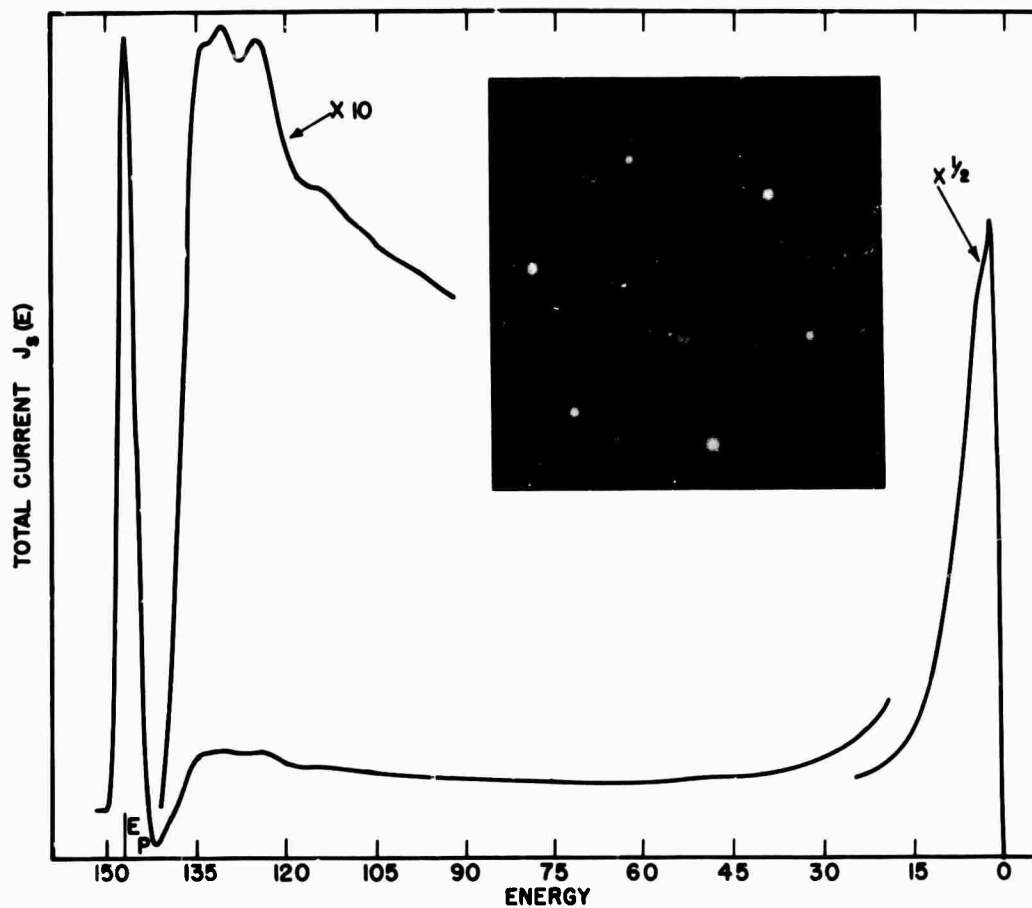


Fig. 31 - Low energy electron diffraction pattern and secondary electron energy distribution curve for an aluminum (111) surface. The curve includes a peak indicating that the elaborate steps used to prepare an entirely clean surface were not quite successful. This observation illustrates one of the many challenges of state-of-the-art surface physics and surface chemistry.

The abstracts are arranged in the following pages by institutions, commencing with The Boeing Company, followed by the universities (alphabetically), and finally the Naval Research Laboratory.

## The Boeing Company

## USE OF PRECRACKED SPECIMENS IN STRESS-CORROSION TESTING OF HIGH STRENGTH ALUMINUM ALLOYS

M. V. Hyatt

## Objective

To establish the V-K curves (stress-corrosion crack velocity versus applied crack tip stress intensity) for several high strength commercial aluminum alloys, and to compare the rating of the alloys based on this data with the ratings established from smooth specimen time to failure data.

## Approach

The V-K curves were obtained using bolt-loaded, double cantilever beam (DCB) specimens intermittently wetted with an aqueous 3.5% NaCl solution. Alloys and tempers tested were 7079-T651, 7079-T651 + 6 hr/325°F, 7075-T651, 7075-T7351, 7175-T66, 7175-T736, 7178-T76, AZ74.61, X7080-T7, 7039-T64, 7049-T7, 2024-T351, 2024-T4, 2024-T851, 2014-T451, 2014-T651, 2219-T37.

## Achievements

The V-K curves showed a double slope behavior. At lower crack tip stress intensities the crack velocities were highly dependent on  $K_I$ , whereas at the higher  $K_I$  levels crack velocities were nearly independent of the applied crack tip stress intensity. Maximum crack velocities ranged from  $4 \times 10^{-5}$  in./hr for the highly susceptible 7079-T651 to  $1 \times 10^{-5}$  in./hr for the highly resistant 7075-T73. Although crack velocities often continued to decrease with decreasing  $K_I$  level, true  $K_{Isc}$  values ( $K_I$  levels below which growth ceases) were not observed for any alloy tested. Rankings of the various alloys based on the V-K curves agreed with established rankings based on smooth specimen time to failure data. In many cases the V-K curves provided more discriminating data than is available from smooth specimen time to failure tests. For example, at the higher  $K_I$  levels stress-corrosion crack growth rates in 7079-T651 were one to two orders of magnitude faster than in 7075-T651 even though both alloys show similar behavior in the standard smooth specimen, alternate immersion test.

A relationship between the smooth specimen stress-corrosion threshold stress from time to failure data and the V-K curves is presented.

## Publications

"Use of Precracked Specimens in Stress-Corrosion Testing of High Strength Aluminum Alloys," M. V. Hyatt, Boeing Document No. D6-24466, November 1969; submitted to Corrosion

## The Boeing Company

**USE OF PRECRACKED SPECIMENS IN SELECTING HEAT TREATMENTS FOR STRESS-CORROSION RESISTANCE IN HIGH STRENGTH ALUMINUM ALLOYS**

M. V. Hyatt

**Objective**

To establish the V-K curves (stress-corrosion crack velocity versus applied crack tip stress intensity) for the alloy 7075 after various overaging heat treatments between T6 and T73.

**Approach**

The V-K curves were obtained using bolt loaded double cantilever beam (DCB) specimens intermittently wetted with an aqueous 3.5% NaCl solution. Three different techniques were employed. Two techniques used single DCB specimens containing aging gradients along their lengths. The third technique used multiple DCB specimens, each one having a different heat treatment.

**Achievements**

Results from each technique showed that for the 7075 alloy, overaging to an electrical conductivity of at least 38% IACS is necessary before stress-corrosion crack growth rates approach those of 7075-T73. Stress-corrosion performance was established most rapidly using multiple DCB specimens. After only a few hundred hours the crack growth characteristics were sufficiently established using this technique that the different heat treatments could be rated against the known performance of 7075 in the T6 and T73 tempers.

**Publications**

"Use of Precracked Specimens in Selecting Heat Treatments for Stress-Corrosion Resistance in High Strength Aluminum Alloys," M. V. Hyatt, Boeing Document No. D6-2447, November 1969; submitted to Corrosion

## The Boeing Company

**EFFECT OF RESIDUAL STRESSES ON STRESS-CORROSION CRACK GROWTH RATES IN ALUMINUM ALLOYS**

M. V. Hyatt

**Objective**

To determine the effects of quenched-in residual stresses on the behavior of pre-cracked double cantilever beam (DCB) stress-corrosion specimens of high strength aluminum alloys 7075, 7175, and 7079.

**Approach**

The V-K curves (stress-corrosion crack velocity versus applied crack tip stress intensity) were obtained using bolt loaded DCB specimens intermittently wetted with an aqueous 3.5% NaCl solution. Tests were conducted on specimens containing quenched-in residual stresses and on specimens which had been stress relieved after quenching by stretching or explosive shocking.

**Achievements**

Large differences in crack front profiles were observed between specimens with and without residual quenching stresses. Severe crack front bowing occurred in non-stress relieved specimens. In addition the crack opening displacement in the non-stress relieved specimens was effectively increased at the crack tip by the bowing apart of the two DCB specimen arms as the stress-corrosion crack propagated through the material. These effects result primarily from the residual compressive stresses on the surfaces of the non-stress relieved specimens. Both the crack front bowing and the bowing apart of the DCB specimen arms cause errors in the calculated  $K_I$  levels. These problems were eliminated by stress relieving DCB specimens after quenching. This work underlines the fact that residual quenching stresses in actual parts susceptible to stress-corrosion cracking not only increase chances of initiating stress-corrosion cracks, but also play an important role in increasing average growth rates. This can result from the increased crack opening displacement (and therefore  $K_I$  level) at the crack tip due to deflections caused by the residual stresses.

**Publications**

"Effect of Residual Stresses on Stress Corrosion Crack Growth Rates in Aluminum Alloys," M. V. Hyatt, Boeing Document No. D6-24469, November 1969; submitted to Corrosion

**The Boeing Company****EFFECTS OF SPECIMEN GEOMETRY AND GRAIN STRUCTURE ON STRESS-CORROSION CRACKING BEHAVIOR OF ALUMINUM ALLOYS****M. V. Hyatt****Objective**

To establish the V-K curves (stress-corrosion crack velocity versus applied crack tip stress intensity) for aluminum alloy double cantilever beam (DCB) specimens with various side grooves, grain structures, and thicknesses.

**Approach**

DCB specimens with various side grooves, grain structures, and thicknesses were tested in an environment consisting of intermittent wetting with aqueous 3.5% NaCl solution.

**Achievements**

Branch cracking and arm breakoff may occur during testing of DCB specimens of aluminum alloy materials with equiaxed grain structures. Side grooves on DCB specimens had a negligible effect on crack growth rate data. Double cantilever beam specimens from materials as thin as 0.050 in. can be successfully tested.

**Publications**

"Effects of Specimen Geometry and Grain Structure on Stress Corrosion Cracking Behavior of Aluminum Alloys," M. V. Hyatt, Boeing Document No. D6-24470, November 1969; submitted to Corrosion

The Boeing Company

## **EFFECT OF QUENCHING RATE ON STRESS-CORROSION CRACK GROWTH RATES IN 2024-T4 ALUMINUM**

**M. V. Hyatt**

### **Objective**

To determine the effect of quenching rate on the V-K curves (stress-corrosion crack velocity versus applied crack tip stress intensity) for 2024-T4.

### **Approach**

Specimens of 2024 were resolution treated, quenched at two different rates, and naturally aged to the T4 temper.

The V-K curves were obtained using bolt loaded double cantilever beam (DCB) specimens intermittently wetted with an aqueous 3.5% NaCl solution.

### **Achievements**

Actual stress-corrosion crack growth rates were higher in the more slowly quenched 2024-T4 alloy. This behavior agrees with trends observed by others based on percent loss in tensile strengths of pre-exposed specimens which have been quenched at different rates.

### **Publications**

"Effect of Quenching Rate on Stress-Corrosion Crack Growth Rates in 2024-T4 Aluminum," M. V. Hyatt, Boeing Document No. D6-24471, November 1969; submitted to Corrosion

## The Boeing Company

## DEVELOPMENT OF A HIGH STRENGTH, STRESS-CORROSION RESISTANT ALUMINUM ALLOY FOR USE IN THICK SECTIONS

M. V. Hyatt and H. W. Schimmelbusch

## Objective

To develop a new high strength Al-Zn-Mg-Cu alloy with a smooth specimen stress-corrosion threshold stress of 25 ksi, good toughness and fatigue properties, and a quench sensitivity such that the properties can be maintained at a high level in thick plate and forgings.

## Approach

To meet the strength goals an alloy with zinc and magnesium contents intermediate between those of 7075 and 7178 was selected. To reduce quench sensitivity the copper content was reduced to about 1.0%, and zirconium and manganese were added in place of chromium which is the normal recrystallization retardant in 7075 and 7178 alloys. The amount of overaging required to meet the stress-corrosion goal was determined using both smooth specimens and precracked double cantilever beam (DCB) specimens. Finally, hand and die forgings, plate, and extrusions of the new alloy were given the selected heat treatment and evaluated to determine mechanical, fracture, fatigue, and stress-corrosion properties.

## Achievements

Mechanical, fracture, and stress-corrosion properties for die forgings of the new alloy (alloy 21) and several other forging alloys are compared in the following table.

Alloy	Thickness (in.)	Minimum longitudinal properties		Longitudinal $K_{Ic}$ range (ksi $\sqrt{\text{in.}}$ )	Short-transverse stress-corrosion threshold (ksi)	
		$F_{tu}$ (ksi)	0.2% $F_{ty}$ (ksi)		3.5% NaCl alternate immersion	Industrial atmosphere
Alloy 21	6.75	69*	60*	30-38*	> 25*	> 25*
7049-T73	5.0	70	60	30-38*	45	?
X7080-T7	6.0	65	57	27-30	25	15
7075-T73	3.0	66	56	27-38	> 47	> 47
7075-T73	6.0	61	51	27-38	> 47	> 47
7175-T736	3.0 max	76	66	27-38	~ 35	?
7075-T6	3.0 max	75	65	25-32	7	14
7079-T6	6.0	72	62	25-32	7	6

\*Estimated values

The mechanical properties of alloy 21 are comparable to those of 7049-T73. The fracture toughness of alloy 21 is as good as or better than that of the other alloys listed. The smooth-specimen short-transverse stress-corrosion threshold appears to be greater than 25 ksi. Test data also indicate that the smooth and notched axial (tension-tension) fatigue properties of alloy 21 are comparable to those of 7075-T6 and 7075-T73.

**Publications**

**"Development of a High-Strength, Stress-Corrosion Resistant Aluminum Alloy for Use in Thick Sections," M. V. Hyatt and H. W. Schimmelbusch, Technical Report AFML-TR-70-109, May 1970, Boeing Document No. D6-60122**



## The Boeing Company

**EFFECT OF EXPOSURE TIME AT 250°F ON STRESS-CORROSION CRACK GROWTH RATES IN 2024-T351 ALUMINUM****M. V. Hyatt and W. E. Quist****Objective**

To determine the degree of sensitization to stress-corrosion cracking of 2024-T351 after exposure at 250°F (a temperature commonly used during curing of adhesively bonded assemblies).

**Approach**

Double cantilever beam (DCB) specimens of 2024-T351 were exposed at 250°F for times up to 300 hours. V-K curves (stress-corrosion crack velocity versus applied crack tip stress intensity) were then obtained in an environment consisting of intermittent wetting with aqueous 3.5% NaCl solution.

**Achievements**

Stress-corrosion crack velocities were observed to increase in specimens which had been exposed for only 2-5 hours at 250°F. Maximum crack velocity increases of about 60% occurred on specimens which had been exposed from 15 to 100 hours.

The Boeing Company

## FUNDAMENTAL ASPECTS OF STRESS-CORROSION CRACKING OF HIGH STRENGTH ALUMINUM ALLOYS

Markus O. Speidel

### Objective

At the Boeing Scientific Research Laboratories experimental and theoretical studies of stress-corrosion cracking in high strength aluminum alloys have three aims: (1) to identify the major influential parameters, that is, the conditions under which stress-corrosion cracks can grow; (2) to compare such conditions with those that cause stress-corrosion cracking in other alloy systems, polymers, and glasses, in an attempt to define their limits of applicability; and (3) to increase our understanding of the basic mechanisms of stress-corrosion crack propagation.

### Approach

With complementary fractography and metallurgical examination, the main effort was concentrated on the measurement of stress-corrosion crack tip velocity as a function of the following parameters.

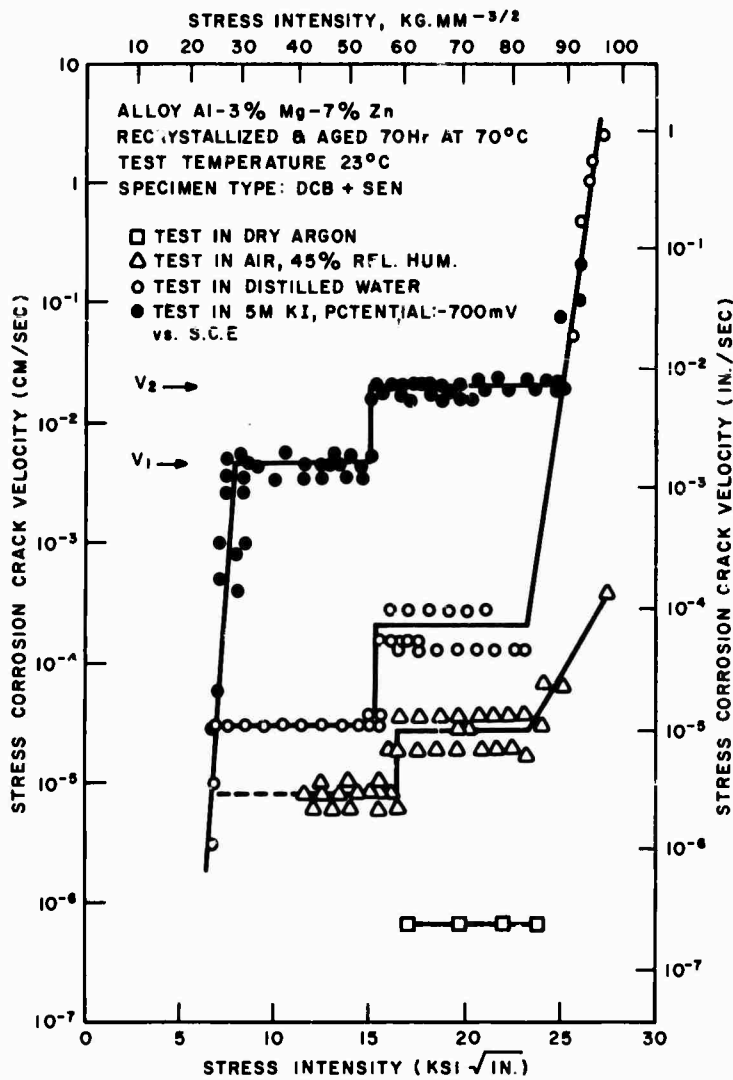
1. Mechanical parameters
  - a) applied crack tip stress intensity
  - b) specimen geometry
2. Environmental parameters
  - a) concentration of halide ions
  - b) concentration of other inorganic anions
  - c) concentration of water in the environment
  - d) presence of various gases
  - e) concentration of organic liquids
  - f) concentration of protons
  - g) presence of other cations
  - h) presence of liquid metal in the crack
  - i) temperature
  - j) viscosity of electrolyte
  - k) electrochemical potential
3. Metallurgical parameters
  - a) aging time
  - b) aging temperature
  - c) alloy concentration
  - d) recrystallization

### Achievements

Crack propagation was shown to be affected by almost all the parameters listed. The first step in each case was to measure the effect of the variation of just one parameter on the velocity while keeping all the other parameters constant at some "reasonable" value. Our data showed that this can lead to quite different results,

depending on the actual value chosen for those parameters that were kept constant. The interdependence of the effects of various parameters on stress-corrosion crack velocity is illustrated in Figs. 1, 2, and 3.

**Effect of Stress on Crack Tip Velocity**—Crack tip stress intensity has a decisive effect on stress-corrosion crack velocity. It can cause the velocity to vary from less than  $5 \times 10^{-9}$  cm/sec to more than 2 cm/sec, a range that exceeds by far the lowest and the highest subcritical crack velocity ever before directly observed in aluminum alloys. Although the slowest cracks took a year to become visible, a movie camera had to be used to record the fastest cracks. Generally, there are three regions of the crack velocity versus stress intensity curve: region I at low stress intensities where the crack velocity is strongly stress dependent; region II at intermediate stress intensities where the crack velocity is independent of stress and which subsequently may show one or two plateaus; and region III at stress



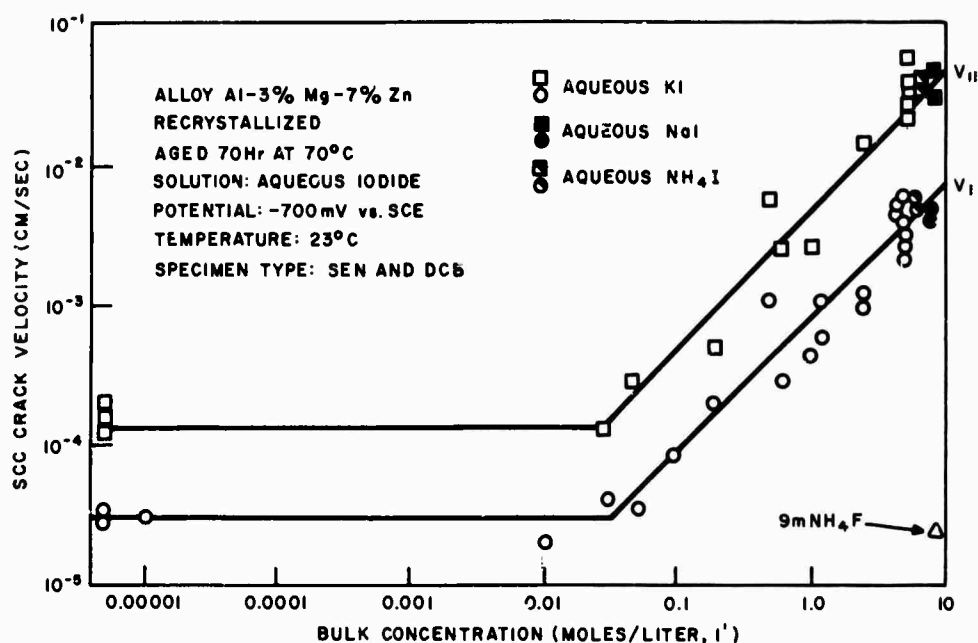


Fig. 2 - The effect of halide ion concentration on SCC crack velocity

intensities close to  $K_{Ic}$  where the velocity again is strongly stress dependent. Commercial aluminum alloys show only regions I and II, but a high-purity alloy showed all three regions, as illustrated in Fig. 1. For the experimental conditions listed in Fig. 1, stress-corrosion crack velocity apparently does not depend on halide ion concentration in regions I and III. Region II, however, is strongly affected by halide ion concentration. This is obvious from both Figs. 1 and 2, which are based on hundreds of tests on self-stressed double cantilever beam specimens and single-edge-notched tension specimens. Thus, there is no simple answer to whether halide ion concentration affects stress-corrosion crack velocity. The answer is no for regions I and III, but yes for region II. Velocity in region I is thought to be kinetically limited. Velocity in region II is thought to be limited by mass transport. The existence of region III is thought to be due to additional mechanical components of crack growth.

**Effect of Halide Ion Concentration on Stress-Corrosion Crack Velocity**—Figure 2 shows the effect of iodide concentration on the two plateau velocities that may be seen in region II in Fig. 1. The linear increase of the plateau velocities at higher iodide concentrations is consistent with the concept of mass transport limited velocity. The constant velocity at low halide ion concentrations can be attributed to water as a stress-corrosion agent. This behavior also occurs in commercial aluminum alloys and is similar for bromide and chloride ions. Fluoride ions, however, do not accelerate stress-corrosion cracking over the rate found in distilled water.

**Effect of Electrochemical Potential on Stress-Corrosion Crack Velocity**—In Fig. 3 it may be seen that the effect of halide ion concentration on region II velocity applies only at a specific electrochemical potential of the specimen and only at a specific pH value of the bulk electrolyte. For example, at a potential of  $E = -1600$  mV, there is no influence whatsoever of iodide concentration on stress-corrosion crack velocity. This is true if the solution is neutral. Under such conditions, the crack propagates even in concentrated solutions with the velocity characteristic of

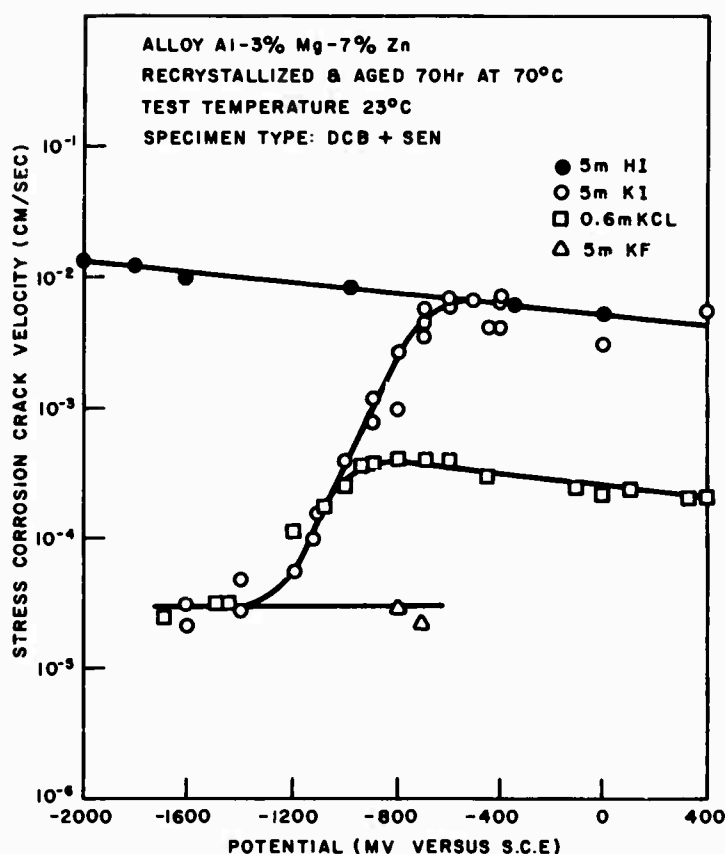


Fig. 3 - The effect of electrochemical potential on SCC crack velocity

propagation in distilled water. (Compare Figs. 1, 2, and 3.) In strongly acidic solutions, however, cathodic protection is impossible, and the crack propagates with the velocity characteristic for propagation in highly concentrated halide solutions. Between the cathodic-protection and the pitting potentials, stress-corrosion crack velocity in neutral  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  solutions increases with potential and finally levels out at rates that are determined by the halide ion concentration. The increase in velocity is attributed to the replacement of  $\text{OH}^-$  ions by halide ions. The leveling off beyond the pitting potential is attributed to the consumption of halide ions on the crack walls.

#### Summary of Other Results—

1. Crack-line-loaded and remote-loaded specimens yield comparable crack velocity versus stress intensity curves.
2. Of 20 anions tested, only  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , and, to a much lesser degree,  $\text{NO}_3^-$  accelerate stress-corrosion crack growth.
3. Ten different cations tested resulted in the same stress-corrosion crack velocity. An exception was  $\text{H}^+$  in the cathodic protection range.

4. Liquid metals cause stress-corrosion crack velocities up to 20 cm/sec and  $K_{I_{sc}}$  as low as 0.8 ksi  $\sqrt{\text{in.}}$ .
5. Solution viscosity is inversely proportional to stress-corrosion crack velocity.
6. Overaging causes not only a reduction in velocity, but also an increase in the limiting stress intensity in region I.
7. Alloys recrystallized to large equiaxed grains show stress-corrosion crack velocities 10 to 100 times faster than commercial alloys with the usual flattened grains.
8. There is no true  $K_{I_{sc}}$  for aluminum alloys. Cracks just slow down at lower stress intensities, but do not stop.
9. In commercial aluminum alloys, no crack growth occurs in gases and organic liquids unless water is present.

## The Boeing Company

**ENVIRONMENTAL FATIGUE CRACK PROPAGATION OF ALUMINUM ALLOYS AT LOW STRESS INTENSITY LEVELS**

J. A. Feeney, J. C. McMillan, and R. P. Wei

**Objective**

The objectives of the study were:

- a) To evaluate the performance of commercial aluminum alloys when subjected to cyclic stresses in corrosive and "mild" environments.
- b) To correlate the data within the framework of linear-elastic fracture mechanics using the crack tip stress-intensity factor  $K$  to characterize the crack driving force.
- c) To examine fatigue crack growth rates at low values of stress intensity factor where the mechanical aspects of the fatigue process are less dominant.
- d) To correlate the rate of fatigue crack propagation in a particular environment and at a particular  $K$  level with the fracture topography.

**Approach**

Corrosion fatigue experiments were conducted on aluminum alloys 7178-T6, 7075-T6, and 2024-T3. Panels of dimensions  $24 \times 9 \times 0.16$  in. were cyclic stressed by wedge force and remote loading techniques. Five different environments were studied: desiccated argon (10 ppm  $H_2O$ ), dry air ( $< 10\%$  relative humidity), wet air ( $> 90\%$  relative humidity), distilled water, and 3.5% NaCl solution. Data was plotted as  $\log \Delta K$  versus  $\log da/dN$ .

**Achievements**

Wedge force loading and remote loading techniques were found to be compatible under the test conditions used in this investigation. When the data was plotted as  $\log \Delta K$  versus  $\log da/dN$ , two transition regions were exhibited:

- a) The transition at high levels of  $\Delta K$  was environmentally controlled and reflected a change-over from a plane strain to plane stress mode of propagation.
- b) The transition at low levels of  $\Delta K$  was not environmentally controlled and reflected some intrinsic property of the material.

The frequency effect was found to be controlled mostly by the environmental influence and was not an intrinsic property of the material. The effects of the environments on the rate of fatigue crack propagation were:

- a) Environmental sensitivity was most pronounced at low levels of cyclic amplitude of stress intensity  $\Delta K$ .

- b) Alloy 2024-T3 was relatively insensitive to the mild environments when compared to dry air, whereas 7075-T6 and 7178-T6 showed a pronounced acceleration in fatigue crack growth rate when tested in either wet air or distilled water.
- c) All three alloys exhibited a marked susceptibility to environmentally enhanced fatigue crack growth rate in 3.5% NaCl solution. In contrast to 2024-T3 and 7075-T6, however, fatigue crack growth of 7178-T6 was faster in distilled water than in 3.5% NaCl solution.

The most pertinent fractographic observations were:

- a) Ductile striations were not observed at growth rates ( $da/dN$ ) less than  $250 \text{ \AA}/\text{cycle}$ .
- b) Cleavage-like fracture, stepwise growth, and rippled facet fracture were the most pronounced transgranular fracture modes at crack growth rates below  $10 \text{ \mu in.}/\text{cycle}$ .
- c) Cleavage-like fracture appeared to be environmentally controlled and was more pronounced the less ductile the material.
- d) Intergranular fracture was the most common fracture process in specimens of 2024-T3 and 7178-T6 tested in 3.5% NaCl solution at low  $\Delta K$  levels. In 7075-T6, however, intergranular fracture did not occur at any  $\Delta K$  level.
- e) Environmental sensitivity at relatively higher  $\Delta K$  levels was not always associated with a change in fracture mode from ductile striation formation to brittle striation formation. In 2024-T3, for example, brittle striations did not form in any of the environments used in the investigation.

#### Publications

"Environmental Fatigue Crack Propagation of Aluminum Alloys at Low Stress Intensity Levels," J. A. Feeney, J. C. McMillan, and R. P. Wei, Boeing Document No. D6-60114, May 1969 (DDC Accession No. AD 692166); published in Metallurgical Transactions 1: 6, June 1970, p. 1741

#### Presentations

"Environmental Fatigue Crack Propagation of Aluminum Alloys at Low Stress Intensity Levels" by J. A. Feeney, ASM/WESTEC Meeting, Los Angeles, May 1969



## The Boeing Company

## IMPROVING THE TOUGHNESS AND STRESS-CORROSION RESISTANCE OF AFC 77

D. Webster

## Objective

In the past five years the strength of stainless steels has been improved to the point where they are competitive on a strength-to-weight basis with low alloy steels and alloys of titanium and aluminum. The strongest stainless steel available is AFC 77 which contains 0.15C, 14.5Cr, 5.0Mo, 0.5V, and 13.5Co. In spite of its high strength, this alloy has not found widespread use because of its low toughness and stress-corrosion resistance. The objective of this study was to improve the toughness and stress-corrosion resistance of AFC 77.

## Approach

New heat treatments and thermomechanical processes were used. The three most promising techniques were as follows:

1. In the first process, heat treatment is controlled to ensure that a small amount of austenite remains after heat treatment. The tough austenite diverts or stops a growing crack so that a large amount of energy is necessary for fracture; in other words, the material has a high fracture toughness. AFC 77 is normally considered to have a fully martensitic structure, but there is an increasing tendency for austenite to be retained as the austenitizing temperature is increased. This happens because the stability of the austenite is related to the alloy content of the matrix, which is greater at high austenitizing temperatures due to increased solution of undissolved carbides and intermetallic compounds. An upper limit on the austenitizing temperature is set by the formation of delta ferrite at about 2100°F. In order to be an efficient crack stopper, it is not only necessary that the second phase be tough, but it must also be well dispersed. The dispersion of austenite is produced automatically during the martensite transformation as new martensite needles repeatedly subdivide the areas of austenite in which they form. A modification of the above technique which allows the retained austenite content to be increased has recently been developed. In this technique higher than normal austenitizing temperatures which are inside the austenite + delta ferrite phase field are used. The delta ferrite is then transformed to austenite at lower temperatures after which the normal heat-treatment practice is followed.
2. A new grain refinement process forms the basis of the second technique. In this process the annealed steel is cold rolled at least 35% in the final stages of manufacture and then re-annealed before delivery to the user. While still in the annealed condition, fabrication of the part is completed and then a normal hardening treatment is given which, because of the prior deformation, will develop a refined grain structure. The explanation for the grain refinement is as follows: The cold rolling ruptures the interface between the hard carbide particles and the matrix and causes voids to form around the particles. These voids, which are stable in the austenite at temperatures up to 1875°F, interact with moving grain boundaries at the austenitizing temperature, resulting in a marked refinement of austenite grain size.

3. The third technique, which involves the strain aging of material containing retained austenite, produces the best combination of strength, toughness, and stress-corrosion resistance. In this process the material is austenitized at a temperature high enough to produce retained austenite, tempered at 500°F, and then strained 10-20% by cold rolling. A second tempering treatment in the range 500°-1000°F is then given to develop tensile strengths from 280,000 psi to 330,000 psi. Because a substantial proportion of the retained austenite remains after strain aging, a high level of fracture toughness is maintained.

#### Achievements

Using the PH stainless steels as a base, the techniques described above have increased the strength level at which a given toughness ( $K_{Ic}$ ) can be maintained from the normal 190-230 ksi range to the 310-330 ksi range for strain aged material or the 250-290 ksi range for non-strain aged material. Similar increases in strength level for equivalent stress-corrosion resistance ( $K_{Isc}$ ) is achieved by these techniques. For example, strain-aged AFC 77 sheet with a yield strength of 277 ksi and an ultimate strength of 288 ksi has a  $K_{Isc}$  of 90 ksi√in.

#### Publications

"The Use of Deformation Voids to Refine the Austenite Grain Size and Improve the Mechanical Properties of AFC 77," D. Webster, Boeing Document No. D6-23870, 1969 (DDC Accession No. AD 687724); also Trans. ASM Quarterly 62, Sept. 1969, p. 759

"The Stress Corrosion Resistance and Fatigue Crack Growth Rate of a High Strength Martensitic Stainless Steel AFC 77," D. Webster, Boeing Document No. D6-23973, 1969 (DDC Accession No. AD 695794)

"Stainless Steels Can Be Strong and Tough," D. Webster, Boeing Document No. D6-24379, 1969 (DDC Accession No. AD 695795); also Space/Aeronautics, Sept. 1969, p. 83

"Effect of Grain Refinement on Mechanical Properties of 4340M Steel," D. Webster, Boeing Document No. D6-25220, Feb. 1970

## The Boeing Company

## THE EFFECT OF SILICON ON THE STRESS-CORROSION RESISTANCE OF LOW ALLOY HIGH STRENGTH STEELS

C. S. Carter

## Objective

Silicon modified 4340 steel has exhibited superior service performance to 4340 at the 260-280 ksi ultimate strength range. The purpose of this investigation was to determine if this could be attributed to a beneficial effect of silicon on the stress-corrosion resistance of low alloy type steels.

## Approach

Five 100 lb. heats of 4340 containing 0.09, 0.54, 1.08, 1.58, and 2.15 percent silicon were prepared by vacuum melting. The fracture toughness  $K_{Ic}$ , stress-corrosion threshold  $K_{Isc}$ , and stress-corrosion crack velocity characteristics were determined for each heat for two ultimate tensile strength ranges: 220-240 ksi and 280-300 ksi. Commercial heats of 4340 and 4340 modified were also evaluated. Stress-corrosion tests were conducted in 3.5% NaCl solution.

## Achievements

Silicon did not improve the threshold stress intensity  $K_{Isc}$ . However, in the 280-300 ksi strength range the stress-corrosion crack velocity was significantly decreased when the silicon content exceeded 1.5%. In the lower strength range the stress corrosion was reduced by increasing the silicon content. Strength level had a significant effect on the kinetics of stress-corrosion crack growth. In the highest strength range the velocity was proportional to the crack tip stress intensity. On the other hand, the velocity was constant over a wide range of stress intensity when the steels were tempered to 220-240 ksi.

## Publications

"The Effect of Silicon on the Stress-Corrosion Resistance of Low Alloy High Strength Steels," C. S. Carter, Boeing Document No. D6-23872, March 1969; (DDC Accession No. AD 687726); published in Corrosion 25, 1969, p. 423

## Presentations

"The Effect of Silicon on the Stress-Corrosion Resistance of Low Alloy High Strength Steels" presented by C. S. Carter at ASM/WESTEC Meeting, Los Angeles, March 1969

The Boeing Company

## STRESS-CORROSION CRACK BRANCHING IN HIGH STRENGTH STEELS

C. S. Carter

### Objective

To establish the cause of stress-corrosion crack bifurcation in high strength steels.

### Approach

Stress-corrosion crack morphology was determined in several high strength steels loaded in 3.5% aqueous sodium chloride and related to the applied stress intensity and velocity characteristics of the materials.

### Achievements

It has been established that the criteria for crack branching are an essentially constant crack velocity (i. e., independent of stress intensity) and the attainment of a critical stress intensity level,  $K_{IB}$ . These criteria must be achieved simultaneously for bifurcation. The stress intensity of branching has been empirically expressed as  $K_{IB} \sim (2-4) K_{I_{SCC}}$  and is in good agreement with a branching criteria proposed by Anthony and Congleton. However, a more applicable relationship appears to be  $K_{IB} = 2 K_{I_m}$  where  $K_{I_m}$  is the minimum stress intensity for constant crack velocity.

This study has also shown that the stress-corrosion curve of  $K_{I_i}$  versus time to failure quantitatively reflects the crack velocity characteristics. For constant crack velocity the time to failure shows only a slight dependence on  $K_{I_i}$ , provided that the ratio of initial crack length to specimen width is similar for the specimens used to construct the stress-corrosion curve. Similarly, when the velocity is dependent upon stress intensity the time to failure shows a marked dependence on  $K_{I_i}$ . A simple technique, using pairs of dissimilar size specimens, has been devised to quantitatively determine the constant crack velocity and eliminate the incubation time variable.

There is no correlation between  $K_{I_{SCC}}$  and the crack velocity in the region of stress intensity independence.

### Publications

"Stress Corrosion Crack Branching in High Strength Steels," C. S. Carter, Boeing Document No. D6-23871, March 1969 (DDC Accession No. 687725); to be published in Journal of Engineering Fracture Mechanics

"Crack Extension in Several High Strength Steels Loaded in 3.5% Sodium Chloride Solution," C. S. Carter, Boeing Document No. D6-19770, 1967 (DDC Accession No. AD 685377)

### Presentations

"Stress Corrosion Crack Branching in High Strength Steels," presented by C. S. Carter at National Symposium on Fracture Mechanics, Lehigh University, August 1969

## The Boeing Company

## THE EFFECT OF HEAT TREATMENT ON THE FRACTURE TOUGHNESS AND SUB-CRITICAL CRACK GROWTH CHARACTERISTICS OF A 350 GRADE MARAGING STEEL

C. S. Carter

## Objective

To determine the effect of heat-treatment variables on a recently introduced 350 grade steel and establish its potential for structural application.

## Approach

The 350 grade steel (nominal composition 18.5Ni, 12Co, 4.6Mo, 1.4Ti) was obtained in billet and bar form. The optimum solution treatment was initially established and the effect of aging on stress-corrosion resistance in 3.5% NaCl solution and on fracture toughness was determined.

## Achievements

A double solution anneal at 1700°F/1500°F gave the best combination of properties. When aged at temperatures below 900°F the subcritical crack growth resistance was so low that growth occurred in unnotched tension specimens loaded at slow strain rates in laboratory air. Reduced crack growth resistance at low aging temperatures appears to be a characteristic of the 18% Ni maraging system and is possibly related to the precipitate distribution. Aging at, and above, 900°F increased  $K_{I_{SCC}}$  and reduced the subcritical crack growth rate. Austenite reversion occurred at aging temperatures exceeding 1000°F (aging time 3 hours) and significantly reduced strength. However, the fracture toughness only slightly improved.

Aging to peak strength gave ultimate tensile strength values within the range 335-347 ksi. The fracture toughness  $K_{I_C}$  and stress-corrosion threshold  $K_{I_{SCC}}$  at this strength level were 35 and 10 ksi  $\sqrt{\text{in.}}$  respectively. Because of this low fracture toughness the risk of brittle fracture in service will be greater than with currently used ultrahigh strength steels.

## Publications

"The Effect of Heat Treatment on the Fracture Toughness and Sub-Critical Crack Growth Characteristics of a 350 Grade Maraging Steel," C. S. Carter, Boeing Document No. D6-22978, June 1969 (DDC Accession No. AD 692165); published in Metallurgical Transactions 1, 1970, p. 1551

## The Boeing Company

## THE INFLUENCE OF PRE-STRESSING ON THE STRESS-CORROSION RESISTANCE OF DEFECT-CONTAINING HIGH STRENGTH STEELS

C. S. Carter

## Objective

To determine the effect of pre-stressing on the stress-corrosion resistance of high strength steels containing cracks.

## Approach

Fatigue precracked single-edge notch specimens of 4340 (project alloy heat treated to 194 ksi yield strength) and 300 grade maraging steel were pre-loaded in air to selected stress intensity levels within the range 0-90%  $K_{Ic}$  (72 ksi  $\sqrt{\text{in.}}$ ). After unloading, a stress-corrosion curve of  $K_{Ii}$  versus time to failure and the threshold stress intensity level  $K_{Isc}$  were determined for each pre-load condition in 3.5% aqueous sodium chloride solution.

## Achievements

Without pre-load, the  $K_{Isc}$  for the 4340 steel was 8 ksi  $\sqrt{\text{in.}}$ . The threshold increased in proportion to the pre-load stress intensity level such that  $K_{Isc}$  exceeded 25 ksi  $\sqrt{\text{in.}}$  with a pre-load of 90%  $K_{Ic}$ . The time to failure for applied stress intensities ( $K_{Ii}$ ) above the threshold(s) was independent of the pre-load. Tests on maraging steel suggest pre-loading has little effect on  $K_{Isc}$  in this steel. The observations are attributed to compressive stresses at the crack tip which result from the pre-loading.

## The Boeing Company

## THE STRESS-CORROSION RESISTANCE OF PRECIPITATION HARDENING STAINLESS STEEL IN 3.5% SODIUM CHLORIDE SOLUTION

C. S. Carter, D. A. Farwick, A. M. Ross, and J. M. Uchida

## Objective

To determine the stress-corrosion resistance of commercially available high strength precipitation hardening stainless steels in 3.5% aqueous sodium chloride solution using precracked specimens. There were three goals: (1) to provide design oriented information, (2) to determine the influence of microstructure and alloy content, and (3) to compare the precracked specimen results with reported smooth specimen data and known service performance.

## Approach

The following stainless steels, mostly in bar form, were evaluated: 17-7PH, PH15-7Mo, 17-4PH, PH13-8Mo, AM355, AM362, AM364, and Custom 455. Most of the steels were evaluated in two heat-treatment conditions (maximum strength and overaged). Stress-corrosion curves and threshold  $K_{Isc}$  values were determined. Fractographic and microstructural studies were conducted for alloy/heat-treatment condition.

## Achievements

The semi-austenitic steels 17-7PH and PH15-7Mo were particularly sensitive to stress-corrosion cracking. Most of the martensitic steels were very resistant, with  $K_{Isc}/K_{Ic}$  values close to unity. An exception to this was AM362 which was very susceptible. The steels with low  $K_{Isc}$  values had low fracture toughness, and all stress-corrosion cracks propagated in an intergranular manner. The effect of alloy content could not be clearly defined. However, it did appear that a high Cr/Ni ratio and titanium had an adverse effect on fracture toughness. Overaging significantly increased fracture toughness and stress-corrosion resistance. Correlation with service performance was good except in one case; the alloy 17-4PH showed no stress-corrosion susceptibility whereas service failures have been experienced. Comparison of precracked specimen and smooth specimen data for certain materials revealed discrepancies. These are explained in terms of the necessity for pit development in the smooth specimens.

## Publications

"Stress Corrosion Properties of High-Strength Precipitation Hardening Stainless Steels in 3.5% Aqueous Sodium Chloride Solution," C. S. Carter, D. G. Farwick, A. M. Ross, and J. M. Uchida, Boeing Document D6-25219, February 1970

## The Boeing Company

DEVELOPMENT OF TEST SPECIMENS AND TEST PROCEDURES FOR  
COMMERCIAL STEELS

H. R. Smith

## Objective

Stress-corrosion testing techniques have not been standardized to the extent that data are reproducible from facility to facility. It is also difficult for a specification to gain acceptance if it contains procedures which are time-consuming and costly. Therefore it is desirable to find new specimens which will yield results rapidly. The objectives of the programs described in this section were to determine the variables that influence the level of  $K_{Isc}$  in steel alloys and to study the feasibility of using a more effective system to assess susceptibility to stress-corrosion cracking.

## Approach

An important consideration affecting the determination of  $K_{Isc}$  appears to be the state of stress at the crack tip as it is affected by the thickness of the specimen. Specimens varying in thickness from 0.005 in. to 1.0 in. were prepared and tested in sodium chloride solution to find  $K_{Isc}$ . The tapered double cantilever beam configuration was investigated as a means of obtaining crack growth rates in salt solution at constant  $K_I$  levels. The reason for performing this test was to obtain rates in short periods of time and to obtain  $K_{Isc}$  by extrapolating the curve of  $K_I$  as a function of crack growth rate to zero rate. A characteristic of this specimen is that the  $K_I$  level does not change as the crack extends, and the crack growth rate can be established over a measured amount of extension. Other systems require that the rate be determined by finding the slope at any point on the curve of crack length as a function of time, a process which may introduce errors.

## Achievements

It was found that  $K_{Isc}$  of 4340 steel alloy heat treated to a tensile strength of 205 ksi increases with decreasing thicknesses. The minimum value of  $K_{Isc}$  occurred when the thickness was equal to or greater than  $2.5 (K_{Isc}/F_{tys})^2$ .

Curves of crack growth rate as a function of  $K_I$  were obtained for 4340M, Maraging 250, and 9Ni-4Co-0.45C (bainitic) steels using the tapered double cantilever beam specimen. When these curves were extrapolated to zero growth rate, the equivalent  $K_I$  values agreed with  $K_{Isc}$  values reported for these materials. The maximum time required for a complete determination was two weeks.

## Publications

"A Note on Stress Corrosion Cracking Rates," by S. Mostovoy, H. R. Smith, R. G. Lingwall and E. J. Ripling, to be published in Engineering Fracture Mechanics



**Presentations**

**"A Note on Stress Corrosion Cracking Rates," by S. Mostovoy, H. R. Smith, R. G. Lingwall and E. J. Ripling, presented at the National Symposium on Fracture Mechanics, Lehigh University, August 25, 1969**

## The Boeing Company

## DEVELOPMENT OF TEST SPECIMENS AND PROCEDURES FOR MEASURING THE STRESS-CORROSION CRACKING CHARACTERISTICS OF TITANIUM ALLOYS

H. R. Smith

## Objective

There has been a serious inability to collate stress-corrosion data generated in different laboratories by different techniques. Precracked specimens, amenable to analysis by fracture mechanics, may provide the means by which standardization can be achieved. The objective of this program was to investigate the variables that influence the determination of the threshold stress intensity factor for ( $K_{Isc}$ ) of titanium alloys.

## Approach

- a) To establish that the fracture mechanics parameter,  $K_I$ , was more suitable in describing SCC than was net- or gross-section stresses.
- b) To optimize specimen design and testing procedures by investigating the variables which affect the determination of the threshold stress intensity factor,  $K_{Isc}$ .

The environment was aqueous 3.5% sodium chloride solution.

## Achievements

Center cracked panels were subjected to sustained wedge force loading and exposed to an aqueous corrosive environment. This type of experiment provides a unique resolution of whether stress-corrosion cracking depends on  $K_I$  or net-section stress, because crack extension causes a decrease in  $K_I$ , but an increase in net-section stress at the crack tip. Dependency on  $K_I$  was proved when changes in crack growth rate followed similar changes in  $K_I$ .

The effect of thickness on  $K_{Isc}$  of a Ti-6Al-4V alloy was determined from sets of specimens varying in thickness from 0.010 in. to 0.750 in. obtained by machining to size. Over this range,  $K_{Isc}$  was insensitive to thickness.  $K_{Isc}$  was determined from sets of mill annealed Ti-8Al-1Mo-1V and Ti-6Al-4V specimens which had been precracked at different stress levels varying from 15 to 80% of  $K_{Ic}$ . The pre-cracking stress level caused changes in  $K_{Isc}$  that were no greater than those usually attributed to scatter.

A successful comparison of data generated at two different laboratories has also been achieved (3). Single-edge cracked specimens of Ti-8Al-1Mo-1V mill-annealed plate were evaluated by cantilever bending at NRL and by four-point loading at Boeing. In addition, the experiment was further varied at Boeing by adding on aqueous environment before and after loading. The  $K_{Isc}$  values obtained by NRL and Boeing were similar. The electrolyte/loading sequence was repeated for Ti-4Al-3Mo-1V, which is tougher and less susceptible than mill-annealed Ti-8Al-1Mo-1V. Again, similar  $K_{Isc}$  values were obtained. A further series of tests on commercially pure titanium, which is very tough, but susceptible to SCC, indicated lower values for  $K_{Isc}$  when the specimens were loaded in the presence of the electrolyte. Recently, a similar trend has been noticed in alpha and alpha-beta

commercial titanium alloys. Thus, it has been recommended that the specimen always be loaded in the presence of an aqueous environment.

#### Publications

"A Study of Stress-Corrosion Cracking by Wedge-Force Loading," H. R. Smith, D. E. Piper, and F. K. Downey, Boeing Document No. D6-19768, June 1967 (DDC Accession No. AD 661811); also Engineering Fracture Mechanics 1: 1, June 1968, pp. 123-128

"The Relationship Between Test Results and Service Experience," D. E. Piper, Symposium on the Engineering Practice to Avoid Stress-Corrosion Cracking, AGARD Conference Proceedings No. 53, Feb. 1970; Boeing Document No. D6-24473, Oct. 1969

"Stress Corrosion Testing," H. L. Craig, Jr., D. O. Sprowls, and D. E. Piper, to be published as Chapter in ECS Corrosion Monograph Series Book, Corrosion Testing, Edited by W. H. Ailor

#### Presentations

"Quantitative Test Techniques for Environmental Cracking," D. E. Piper, H. R. Smith, and F. K. Downey, presented by D. E. Piper at NACE 23rd Annual Conference, Los Angeles, California, March 13-17, 1967

"A Study of Stress-Corrosion Cracking by Wedge-Force Loading," presented by H. R. Smith at the National Symposium on Fracture Mechanics, Lehigh University, Bethlehem, Pa., June 19-21, 1967

"A Review of Stress Corrosion Testing Methods," presented by D. E. Piper at ASTM Fall Meeting, Atlanta, Georgia, October 1968

"The Relationship Between Test Results and Service Experience" by D. E. Piper, presented during the Symposium on the Engineering Practice to Avoid Stress Corrosion Cracking, 29th Meeting of the Structures and Materials Panel of AGARD, Istanbul, Turkey, Sept. 28, 1969

"The Selection of Precracked Specimens for Characterization of Stress Corrosion," D. E. Piper and H. R. Smith, presented at WESTEC Meeting, Los Angeles, March 11-12, 1970

"Standardization of Test Techniques for Stress Corrosion Cracking," D. E. Piper, presented to Working Group on Stress Corrosion of Structures and Materials Panel of AGARD in Athens, Greece, April 1970

## The Boeing Company

**A METHOD OF MEASURING CRACK GROWTH RATES IN BRITTLE MATERIALS**

N. M. Lowry

**Objective,**

The rate at which a crack progresses is an important parameter which is necessary in understanding the mechanism of stress-corrosion cracking. Previous measurements of crack propagation rate in aqueous environment were tedious and subject to errors of judgment by the observer. The objective of this study was to eliminate these errors and automate the rate measurement.

**Approach**

There are two methods of applying grid conductors: vacuum deposition through masks and selective etching. Selective etching can produce lines as small as 0.0005 in. wide. Selective etching is accomplished by first applying a blanket coating of the resistor material, applying a coating of photoresist, and then exposing the photoresist through a master with a carbon arc to define the grid. The unexposed photoresist is soluble in xylene and the unprotected conductor can be dissolved with a suitable acid. The grid is placed on the surface of the specimen across the anticipated crack path, electrically insulated by oxide films from both metal and corrosive. Electrical resistance of the grid is monitored and indicates the severing of individual elements.

**Achievements**

An accurate network of resistors can be prepared with a suitable combination of materials that will provide a reproducible method of measuring the propagation rate of brittle-type fractures in small specimens.

**Publications**

"A Method of Measuring Crack Propagation Rates in Brittle Materials." N. M. Lowry, O. K. Mulkey, J. M. Kuronen, and J. W. Bieber, Boeing Document D6-60072, May 1967 (DDC Accession No. AD 661814)

## The Boeing Company

**TERMINAL FRACTURE OF TITANIUM ALLOYS CONTAINING STRESS-CORROSION CRACKS**

C. S. Carter

**Objective**

To confirm that rapid brittle fracture occurred under plane strain conditions when the stress intensity at the tip of a propagating stress-corrosion crack was equal to  $K_{Ic}$ .

**Approach**

Approximately one-hundred precracked single-edge notch specimens of Ti-6Al-4V and Ti-4Al-3Mo-1V previously sustain loaded in 3.5% aqueous sodium chloride solution were examined. The stress intensity at which stress-corrosion was terminated by rapid fracture was established for each specimen and compared with the fracture toughness  $K_{Ic}$  determined by a conventional rising load test.

**Achievements**

Rapid brittle fracture occurred when the stress intensity at the stress-corrosion crack tip was equal to  $K_{Ic}$ . The fatigue precrack in specimens loaded to stress intensities below  $K_{Isc}$  was not affected by the environment. The results provide a justification for estimating  $K_{Ic}$  from broken specimens by this technique.

**Publications**

"Terminal Fracture of Titanium Alloys Containing Stress Corrosion Cracks,"  
C. S. Carter, Boeing Document D6-19771, 1968

## The Boeing Company

## THE STRESS-CORROSION CRACKING OF TITANIUM ALLOYS

M. J. Blackburn and J. C. Williams

## Achievements

The metallurgical and mechanical factors which influence the stress-corrosion cracking (SCC) of titanium alloys in aqueous solutions are considered. It is shown that failures of alpha phase in Ti-Al alloys and in commercial alloy Ti-8Al-1Mo-1V under SCC conditions occur by cleavage on the  $\{10\bar{1}8\}$  -  $\{10\bar{1}7\}$  plane of the hexagonal phase. The general phase structure of these alloys is described and it is shown that the  $\alpha + \alpha_2$  (Ti<sub>3</sub>Al) transformation is of considerable importance in determining susceptibility. In the commercial alloy, the presence of the beta phase and the martensitic phases reduce susceptibility. Results on the binary Ti-Al alloys indicate that the onset of susceptibility to SCC occurs between 4-5% aluminum which correlates with a change from homogeneous to planar dislocation arrangements. The influence of stress on the nucleation and propagation of a crack has been analyzed for precracked specimens using the methods of linear elastic mechanics. From these results several factors which influence the nucleation stage are discussed. It is proposed that for a propagating crack there are two components of fracture, i. e., electrochemical and mechanical. At low alpha phase strength levels or aluminum contents the electrochemical component predominates while at higher strength levels or aluminum contents the mechanical component increases. Some qualitative correlations are made between mechanical properties, deformation structures, fracture mode, and susceptibility to SCC.

## Publications

"Metallurgical Aspects of Stress Corrosion Cracking of Titanium Alloys," by M. J. Blackburn and J. C. Williams, presented at Conference on Fundamental Aspects of Stress-Corrosion Cracking, Ohio State University, September 11-15, 1967; published in Proceedings of Conference, NACE, (1969) p. 620

## The Boeing Company

## RELATIONSHIP BETWEEN COMPOSITION, MICROSTRUCTURE, AND STRESS-CORROSION CRACKING (IN SALT SOLUTION) IN TITANIUM ALLOYS

R. E. Curtis

## Objective

To determine the influence of composition and microstructure on the stress-corrosion cracking (SCC) behavior of titanium and its alloys.

## Approach

Four alpha titanium alloys and nine alpha-plus-beta titanium alloys were characterized to relate phase composition and associated microstructure to SCC in 3.5% aqueous sodium chloride solution. The effect of alpha stabilizers such as oxygen and aluminum, and neutral strengtheners such as tin and zirconium on SCC was determined using commercial alpha alloys. These alloys were also used to examine the influence of grain size, grain morphology, degree of order, and dislocation structure on SCC. The effect of beta stabilizing additions was also investigated using commercial or near-commercial alpha-plus-beta alloys. Both isomorphous stabilizers (Mo and V) and eutectoid stabilizers (Fe, Cu, and Si) were investigated. Microstructural changes were achieved in these alloys by varying heat-treatment conditions and by thermomechanical treatment.

## Achievements

The resistance to SCC was found to be dependent on microstructure for a wide range of titanium alloy compositions and thermomechanical treatments. Alloys that exhibited planar slip in the alpha phase also showed pronounced susceptibility to SCC. Planar slip is characteristic of alloys containing: (1) high oxygen (3800 ppma, Ti-707); (2) aluminum in excess of approximately 6 wt-% (e. g. Ti-6Al-4V, Ti-7Al-2.5Mo, and Ti-8Al-1Mo-1V); or 5 wt-% or greater aluminum and 2.5 wt-% or greater tin (Ti-5Al-2.5Sn and Ti-5Al-5Sn-5Zr). A low oxygen, commercially pure titanium alloy (Ti-50A) deformed more homogeneously and was immune to SCC under the conditions of these tests.

Formation of ordered domains of  $Ti_3Al$  or  $Ti_3(Al, Sn)$  in the alpha phase further restricted slip and increased stress-corrosion susceptibility.

Relative stress-corrosion resistance improved with an increased volume percent beta-phase stabilized by isomorphous-type elements Mo or V or both. This has been attributed to the ability of the beta-phase to arrest stress-corrosion cracks that propagate readily through the alpha phase. However, decomposition of the beta-phase may mitigate the ductile behavior of the phase and markedly reduce the stress-corrosion cracking resistance. For example, precipitation of the omega-phase in the beta phase of the alloy Ti-70 is thought to be responsible for reducing  $K_{Isc}$  from 70 ksi $\sqrt{in.}$  to 54 ksi $\sqrt{in.}$  A large volume fracture of alpha-phase in a beta-phase matrix resulted in similar low threshold values. In alloys containing Cu, or Si, low stress-corrosion properties were attributed to precipitation of alpha-phase and intermetallic compounds  $Ti_2Cu$  or  $Ti_5Si_3$  in the beta-phase.

**Publications**

**"Relationship Between Composition, Microstructure, and Stress-Corrosion Cracking in Titanium Alloys," R. E. Curtis, Boeing Document No. D6-23716, October 1968 (DDC Accession No. AD 685380); also published by R. E. Curtis, R. R. Boyer and J. C. Williams in ASM Transactions Quarterly 62, June 1969, p. 457**



## The Boeing Company

## TITANIUM ALLOY DEVELOPMENT

R. E. Curtis and P. T. Finden

## Objective

To develop high strength titanium alloys with improved resistance to stress-corrosion cracking (SCC) in neutral aqueous solutions.

## Approach

Previous work on commercial and near-commercial titanium alloys has shown that both composition and microstructure have a pronounced effect on stress-corrosion susceptibility. In this program, composition changes which have been shown to be consistent with improved resistance to SCC and improved fracture toughness were studied. Twenty-three experimental compositions have been selected to determine the contribution of individual alloying elements and to establish optimum compositions. The alloys are characterized by reduced Al, added Zr, and a relatively large volume percent beta phase compared to most commercial alpha-beta alloys. The aluminum-zirconium combination has been balanced to maintain alloy strength and avoid formation of the  $\alpha_2$  (Ti<sub>3</sub>Al) phase. Molybdenum and vanadium have been added to stabilize up to 25 volume percent beta. In addition, four beta eutectoid stabilizers, silicon, copper, nickel, and iron, have been added to investigate the conditions of intermetallic compound formation and to determine their effects on mechanical properties. The alloys were cast in 8-lb. ingots and fabricated to 0.5-in. -thick plate.

## Achievements

Experimental alpha-beta alloys have been developed which have improved stress-corrosion resistance and toughness compared with commercial titanium alloys of similar strength. These improvements have been achieved over a ultimate tensile strength range from 140 to 200 ksi. For example, at 150 ksi the experimental alloys were approximately 80% more resistant to SCC and 46% tougher than beta processed Ti-6Al-4V. The most promising alloys contain relatively low aluminum, added zirconium, molybdenum, vanadium and/or iron and limited amounts of silicon or nickel. Small zirconium additions were found to increase strength without reducing either resistance to SCC or fracture toughness. Molybdenum and/or vanadium additions also increased strength, but caused small reductions in SCC resistance and toughness.

The influence of beta eutectoid stabilizers on SCC was dependent on both the amount added and on the kinetics of intermetallic compound formation. Silicon additions within the solubility limit of silicon in beta titanium resulted in maximum fracture properties at a tensile strength of 200 ksi. Similarly, small nickel additions resulted in optimum fracture properties at an intermediate tensile strength level of about 175 ksi. Additions of greater amounts of nickel caused pronounced embrittlement. In thin foil and optical metallographic studies, Ti<sub>2</sub>Ni particles were detected in the higher nickel alloys ranging in diameter from 0.05  $\mu$  to 2  $\mu$ . In contrast to nickel, iron additions exceeding the solubility limit of iron in beta titanium did not cause either compound precipitation or embrittlement. Apparently, the kinetics in this system are sufficiently sluggish to preclude Ti-Fe formation even during a slow furnace cool and subsequent 550°F/25ksi/1000 hr. exposure.

ARPA funds have been limited to the stress-corrosion testing phase of this total titanium alloy development program. Further development of these alloys (i. e., new compositions, scaling-up of ingot size for promising experimental alloys, etc.) is being continued wholly under Commercial Airplane Group funding.

## The Boeing Company

## INFLUENCE OF MICROSTRUCTURE ON THE FRACTURE MODE OF TITANIUM ALLOYS

J. C. Williams, R. R. Boyer, and M. J. Blackburn

## Objective

The recent resurgence of interest in titanium has resulted in the investigation of many aspects of the mechanical, structural, and chemical behavior of titanium alloys. One area of obvious importance is the fracture behavior of titanium alloys and the factors that influence it. An attempt was made to relate observations of fracture behavior and topography to structural and environmental factors.

## Approach

Information on fracture modes at ambient temperatures was obtained using standard techniques of electron fractography. All replicas were prepared by a two-stage technique using cellulose acetate for the first stage and germanium-shadowed carbon for the final stage.

## Achievements

The ductile fracture of alpha, beta, and (alpha + beta) phase alloys was shown to occur predominantly by a microvoid coalescence mechanism, but some examples of more ductile behavior were observed in the relatively pure, low-strength alpha-phase.

There is a continuous change in fracture behavior of the alpha phase: alternating shear at low strengths, microvoid coalescence at intermediate strengths (decreasing dimple size with increasing strength), and cleavage fracture at high strengths. Cleavage fracture of the alpha-phase becomes more prevalent (a) at higher yield stresses, (b) at larger grain sizes, (c) in the presence of a sharp notch, and (d) if slip is localized to planar bands.

The fracture topography of macroscopically brittle beta-phase alloys differs markedly from the cleavage fractures associated with brittle fracture of the alpha-phase. Dimples which in most cases are small and shallow are observed in such alloys. The observed embrittlement is associated with formation of a high-volume fraction of small (100 to 1,000 Å) dispersed omega-phase precipitates.

It is shown that the combined action of stress and an active environment can result in brittle fracture of the alpha-phase or the beta-phase in a variety of alloys. Stress-corrosion cracking failures of the alpha-phase closely resemble cleavage fracture produced in air; furthermore, the various metallurgical factors that promote cleavage also increase susceptibility to stress-corrosion cracking. The structural factors that influence susceptibility of a beta-phase alloy appear to be more complicated, as these alloys are usually in their most ductile condition when susceptible to stress-corrosion cracking. There is some evidence that planar slip is observed in susceptible alloys, which may be one structural parameter of importance. It is suggested, however, that the electrochemical properties of the beta-phase may also be an important factor in determining susceptibility.

**Publications**

**"The Influence of Microstructure on the Fracture Topography of Titanium Alloys,"**  
**J. C. Williams, R. R. Boyer, M. J. Blackburn, Boeing Document No. D6-23622,**  
**June 1968 (DDC Accession No. AD 685379); also ASTM STP 453, Electron**  
**Microfractography (1969)**

**The Boeing Company****STRESS-CORROSION CRACKING OF COMMERCIAL TITANIUM ALLOYS****J. C. Williams****Objective**

Stress-corrosion cracking (SCC) of titanium alloys in salt water environments has recently been the subject of intensive investigations. As a result, the relative susceptibility of many of the commercial alloys has been catalogued, although no attempt has been made to explain the observed differences in susceptibility. Alloys that are susceptible to SCC fail by slow growth of a crack under sustained load, followed by fast fracture when the critical crack length is reached. In this study, attention was focused on explaining the occurrence of cleavage fracture of some titanium alloys in salt water environments in terms of metallurgical factors.

**Approach**

Electron fractography, electron metallography, and thin-foil electron microscopy were employed to study three commercial titanium alloys. Of these alloys, Ti-8Al-1Mo-1V was shown to be the most susceptible, Ti-6Al-4V to be less susceptible, and Ti-4Al-3Mo-1V to be highly resistant to SCC.

**Achievements**

The SCC of Ti-8Al-1Mo-1V and Ti-6Al-4V were shown to occur by cleavage of the alpha-phase and by ductile rupture of the beta-phase.

Evidence was presented to show that the beta-phase or transformed beta-phase act as crack arrestors.

Planar dislocation arrangements were shown to exist in Ti-6Al-4V and Ti-8Al-1Mo-1V, but not in Ti-4Al-3Mo-1V. Variations in susceptibility were qualitatively shown to correlate with the development of such dislocation arrangements.

Generation of large stresses normal to the fracture plane were shown to be associated with planar dislocation arrangements, and these stresses are thought to promote SCC.

**Publications**

"Some Observations on the Stress-Corrosion Cracking of Three Commercial Titanium Alloys," J. C. Williams, Boeing Document No. D6-19553, September 1967 (DDC Accession No. AD 661812); published in ASM Transactions Quarterly 60: 4, Dec. 1967, p. 646

## The Boeing Company

## AQUEOUS STRESS CORROSION IN TITANIUM ALLOYS

D. N. Fager and W. F. Spurr

## Objective

The objective of this study was to determine:

- a) the effect of heat-treatment condition
- b) the necessity for precracking
- c) the tendency for cracks not to grow normal to the principal stress axis and
- d) the effect of thickness on stress-corrosion cracking of titanium alloys.

## Approach

Relatively little was known about the phenomenon of aqueous SCC in titanium alloys at the start of this investigation. The approach was to test a number of alloys in different heat-treatment conditions and to examine failed specimens metallurgically to determine possible reasons for changes in susceptibility. The alloys studied were Ti-8Al-1Mo-1V, Ti-6Al-4V, Ti-4Al-3Mo-1V, Ti-5Al-2.5Sn, and Ti-13V-11Cr-3Al. The effect of specimen orientation relative to the preferred (0001) orientation in a single sheet of Ti-8Al-1Mo-1V was studied extensively. The effect of thickness on susceptibility was studied in Ti-6Al-4V. Numerous attempts were made to obtain SCC effects in smooth specimens.

## Achievements

It was verified that in Ti-8Al-1Mo-1V, Ti-6Al-4V, and Ti-4Al-3Mo-1V the alpha-phase was susceptible and the beta and martensitic phase immune to SCC in aqueous sodium chloride solution. In the alpha-phase fracture must occur near the (0001) plane irrespective of specimen orientation relative to the preferred (0001) planes. It is suggested that this single fracture plane limitation resulted in the influence of stress state on the degree of susceptibility. Fracture of the beta-phase in the alloy Ti-13V-11Cr-3Al was found to occur on or near the (001). In the uniaxial stress state, the beta phase of the Ti-13V-11Cr-3Al alloy was found to be significantly more susceptible than the alpha phase of the Ti-8Al-1Mo-1V alloy.

## Publications

"Some Characteristics of Aqueous Stress Corrosion in Titanium Alloys," D. N. Fager and W. F. Spurr, Boeing Document No. D6-60083, Sept. 1967 (DDC Accession No. AD 661813); published in ASM Transactions Quarterly 61: 2, June 1968, p. 283

## The Boeing Company

## METHANOL CRACKING OF TITANIUM-8Al-1Mo-1V

D. N. Fager

## Objective

Titanium-8Al-1Mo-1V alloy is more sensitive to environmental cracking in methanol than in aqueous 3.5% sodium chloride solution. This was demonstrated when premature failures were obtained in smooth specimens of Ti-8Al-1Mo-1V in methanol, but not in salt solution (at 0.005/min. strain rates). The purpose of this study was to determine whether the greater susceptibility in methanol was due to either metallurgical effects (i.e., a susceptible beta-phase) or to the occurrence of fracture on other planes in the  $\alpha$  phase besides the (0001) plane.

## Approach

In a plate of Ti-8Al-1Mo-1V alloy, specimens of two orientations relative to the (0001) preferred orientation were tested in methanol. Specimens from these orientations (from the same plate) had been previously evaluated in 3.5% NaCl solution.

## Achievements

The crack morphology was shown to be the same for methanol and 3.5% NaCl solution, i.e., in both environments the beta phase was immune and cleavage fracture in the alpha-phase was restricted to near the (0001) plane. Failure in precracked specimens occurs at a lower stress-intensity level in methanol than in salt solution. This is consistent with the difference seen in smooth specimen data. This demonstrates that a lower stress (or strain) is required for cleavage of alpha grains in methanol. An interesting observation is that crack propagation is an order of magnitude slower in methanol than in salt solution. Since the fracture characteristics are identical in both environments, the lower fracture stress in methanol must be a result of the metal-solution interface reaction.

## Publications

"Methanol Cracking of Titanium-8Al-1Mo-1V," D. N. Fager, Boeing Document No. D6-23717, Oct. 1968 (DDC Accession No. AD 685381); published Corrosion Science 10, 1970, pp. 175-177

## The Boeing Company

**PREFERRED ORIENTATION IN TITANIUM-8Al-1Mo-1V**

D. N. Fager

**Objective**

To determine variations in preferred orientation in Ti-8Al-1Mo-1V and the deformation mechanisms responsible for them.

**Approach**

The preferred orientation was varied by altering the processing (i. e., temperature and sequence of rolling). The possible deformation modes contributing to the preferred orientations were then analyzed.

**Achievements**

A processing technique for producing, in titanium sheet, the highest anisotropy possible was developed. A strain-induced transformation is offered as an explanation for the texture produced by this processing. A processing technique for significantly eliminating this high anisotropy was also developed.



## The Boeing Company

**AQUEOUS STRESS-CORROSION SUSCEPTIBILITY OF Ti-8Al-1Mo-1V AS INFLUENCED BY PREFERRED ORIENTATION AND NEAR PLANE STRESS CONDITIONS**

D. N. Fager

**Objective**

Previous work on this program has shown that fracture of the alpha-phase in neutral aqueous solutions is limited to near the basal plane. Because of the anisotropy of fracture in the hcp structure, it was felt that highly textured material should be significantly influenced by the stress state. The purpose of this investigation was to determine the influence of orientation (defined as preferred basal plane orientation relative to specimen orientation) on stress-corrosion susceptibility under near plane stress conditions.

**Approach**

An attempt was made to obtain plane stress conditions by varying (1) specimen thickness, (2) specimen orientation relative to the preferred orientation, and (3) material heat treatment. Susceptibility to aqueous stress corrosion was determined as a function of these variables. Single-edge notched specimens were either loaded in tension or in bending.

**Achievements**

Soon after initiation of this program, it was learned that in thin specimens (0.020 in.) the orientation determined to a large extent whether near plane stress conditions could be approached (i. e., near plane stress could not be obtained in thin specimens independent of orientation) in an intermediate yield strength condition. The susceptibility was found to vary with the orientation such that when near plane stress conditions were approached, a significant decrease was observed. When the material was in a low yield strength condition, the same trend was noted; however, when the material was in an intermediate yield strength condition decrease in susceptibility was found in all orientations. This was consistent with the explanation that plane stress conditions tend to promote immunity.

The importance of this work is that susceptibility to aqueous stress corrosion under near plane stress conditions is much more sensitive to preferred orientation and yield strength level than susceptibility under plane strain conditions. This is shown in the following example: the effect of the ordering transformation in Ti-8Al-1Mo-1V was shown to influence susceptibility significantly in thin specimens (0.020 in.), while only a slight effect was noted in thick specimens (0.40 in.). That is, the only apparent effect of the ordering transformation was to lower the yield stress and thus allow plane stress conditions to be more nearly approached in thin specimens.

An additional complicating factor associated with thin specimens (not necessarily with plane stress conditions) was the difference in susceptibility obtained with different loading techniques. If thin specimens were loaded prior to exposure to the

salt solution environment, a lesser degree of susceptibility was found than if they were loaded after exposure. This was not noted in thick specimens of the same material and orientation.

The variables studies in this investigation can explain in large part the tremendous discrepancies in susceptibility noted among various investigators. In thin specimens, susceptibility is significantly influenced by preferred orientation, relatively small changes in yield strength level with heat treatment ( $\sim 10$  ksi), and the sequence of loading and exposing specimens to salt solution.

## The Boeing Company

**EFFECT OF OXYGEN ON THE MECHANICAL AND STRESS-CORROSION PROPERTIES OF BINARY TITANIUM-ALUMINUM ALLOYS**

G. P. Rauscher

**Objective**

To determine the effect of interstitial oxygen on the phase reactions in titanium-aluminum binary titanium-aluminum alloys, and to evaluate the stress-corrosion susceptibility and mechanical properties of these alloys as a function of alloy content and phase constitution.

**Approach**

Nine titanium-aluminum alloys were investigated—4, 6, and 9 wt-% aluminum in titanium—each at three levels of oxygen content, nominally 0.05, 0.20, and 0.40 wt-% oxygen. Electrical resistivity measurements were utilized to determine the variation of phase transformation temperature with composition. Transmission electron microscopy was employed to determine phase constitution as a function of heat treatment. Tensile and fracture toughness properties for selected heat treatments were determined by conventional means. Stress-corrosion susceptibility was assessed utilizing precracked single-edge notched tensile specimens in 3.5% sodium chloride solution.

**Achievements****a) Phase Reactions**

No ordering reaction ( $\alpha$  -  $Ti_3Al$ ) was observed in the 4 wt-% aluminum alloys. In the 6 wt-% aluminum alloys, short range ordering was observed at temperatures below about 600°C. The 9 wt-% aluminum alloys all exhibited long range order, the critical temperature varying from 805°C in this low-oxygen alloy to 835°C in the high oxygen alloy; oxygen was found to inhibit the rate of formation of  $Ti_3Al$  and also to distort the normal ellipsoidal morphology of  $Ti_3Al$ . The alpha and beta transus temperatures of the alloys studied were elevated as much as 70°C by the addition of 0.40 wt-% oxygen.

**b) Mechanical and Stress-Corrosion Properties**

1. The UTS of the 4 wt-% aluminum alloy was increased from 76 ksi to 125 ksi by the addition of 0.40 wt-% oxygen, while the ductility was reduced from 22 to 15 percent elongation at fracture. Only the 0.40 wt-% oxygen alloy was found to be susceptible to stress-corrosion cracking.
2. The tensile and SCC properties of the 6 wt-% aluminum alloys were not affected by short range ordering. The low oxygen alloy was not susceptible to SCC, whereas the medium and high oxygen alloys exhibited susceptibility. UTS and elongation at fracture varied from 100 ksi and 17%, respectively, in the low oxygen alloy to 133 ksi and 8%, respectively, in the high oxygen alloy.
3. In the as-quenched condition the 9 wt-% aluminum, 0.05 wt-% oxygen alloy exhibited a UTS of 95 ksi, an elongation at fracture of 20%, and a  $K_{Isc}$  of

38 ksi  $\sqrt{\text{in.}}$ . On aging these properties were reduced to 70 ksi, 2% elongation, and 15 ksi  $\sqrt{\text{in.}}$ , respectively. The 0.20 wt-% oxygen alloy exhibited a UTS of 105 ksi and 57 ksi in the quenched and ordered conditions respectively. Ordering also caused the alloy to fail without yielding. Ordering enhanced the crack growth rate in salt solution, but did not alter the value of  $K_{I_{acc}}$ . The 0.40 wt-% oxygen alloy was found to be extremely brittle in all conditions tested.

## The Boeing Company

DISLOCATION STRUCTURES IN TITANIUM-ALUMINUM-OXYGEN TERNARY ALLOYS  
RESULTING FROM CYCLIC STRAINING

R. R. Boyer

## Objective

To determine the effects of oxygen and aluminum contents on the dislocation behavior in titanium for the purpose of gaining an insight into the mechanisms of corrosion fatigue in this system.

## Approach

Aluminum and oxygen additions to titanium are known to promote planar slip when tested in uniaxial tension. The onset of this planar slip mode of deformation has, in turn, been related to stress-corrosion cracking in titanium alloys. It was the purpose of this investigation to determine if these alloying additions had the same effect on the dislocation behavior when deformation occurs by cyclic straining. As the fracture modes of titanium alloys are similar in nature when crack propagation occurs by stress-corrosion cracking or corrosion fatigue, this program was initiated to determine if planar slip might account for, or at least play a role in corrosion fatigue.

The alloys tested had aluminum contents ranging from 0-9 wt-% and oxygen contents ranging from about 500-3000 ppm. Specimens were tested in two different ways, tension-tension and bending fatigue. The bending fatigue specimens were rather crude, making determination of the strains involved very difficult.

After testing the specimens, sections were cut out for thin foil examination and prepared using the window technique as described previously by Blackburn and Williams. They were examined on a Philips EM-200 electron microscope equipped with a goniometer lens with  $\pm 45^\circ$  tilt, a decontamination device, and a precision dark-field attachment.

## Achievements

Specimens of high purity titanium, Ti-2Al, Ti-5Al, and Ti-8Al, were tested in bending fatigue. Deformation in the high purity titanium occurred by slip and twinning. The twins were primarily of the  $\{11\bar{2}2\}$  type while slip was rather homogeneous and  $\langle 11\bar{2}0 \rangle$  in nature. The addition of 2% aluminum eliminates the twinning mode of deformation. The fatigue damage occurs by a homogeneous slip mechanism resulting in a random dislocation distribution. A cell structure is also developed in this alloy. Slip becomes more planar in 5% aluminum alloy, predominantly on prismatic and pyramidal planes. With the titanium-8% Al alloy, slip is still planar with a larger spacing between slip bands and less dislocation debris. Ordering of this alloy further enhances this trend. Heavily deformed regions of the 5% and 8% aluminum alloy show a more general deformation.

The specimens tested in tension-tension (Ti-4Al, Ti-6Al, Ti-9Al with oxygen contents between 0.06 and 0.3 wt-%) show trends similar to those observed in the bending fatigue tests. With higher aluminum and oxygen additions the slip became more planar, the slip-band spacing became wider, and decreasing amounts of dislocation debris are observed. No cell structure or twinning was observed in any of these alloys.

The Boeing Company

# EFFECT OF MICROSTRUCTURE ON THE STRENGTH, TOUGHNESS, AND SUSCEPTIBILITY TO STRESS-CORROSION CRACKING OF A METASTABLE BETA ALLOY Ti-11.5Mo-6Zr-5Sn

J. A. Feeney and M. J. Blackburn

## Objective

The alloy Ti-11.5Mo-6Zr-5Sn, often called Beta III, is a compound-free beta alloy developed by the Crucible Steel Company. The beta-to-alpha reaction is very sluggish in this pseudo-isomorphous system, and 100% beta phase can be retained at room temperature after water quenching. Work to date on Beta III has been mainly limited to characterizing the alloy's formability, weldability, and engineering properties. The purpose of this investigation was to determine the phase transformations which occur in this metastable beta alloy, then relate the contribution of microstructure to the alloy's strength, toughness, and susceptibility to stress-corrosion cracking.

## Achievements

The phase transformations which occurred in Beta III were similar to those which have been reported for binary Ti-Mo alloys containing approximately the same Mo content. Some differences in transformation behavior were observed however, such as the temperature range of stability of the omega phase and the aging characteristics of deformed material.

In the temperature range  $-320^{\circ}\text{F}$  to  $+300^{\circ}\text{F}$ , the Beta III deforms primarily by mechanical twinning and to a lesser extent by slip and stress-induced orthorhombic martensite formation. The twinning system is  $\{332\} \langle 113 \rangle$  and not the common  $\{112\} \langle 111 \rangle$  system observed in most other body-centered-cubic materials. At room temperature, as-quenched structures have a low yield stress, a high ductility, and a high toughness.

The formation of beta + omega structures at aging temperatures such as  $700^{\circ}\text{F}$  results in the progressive increase in yield strength with increasing aging time (and hence increasing omega particle size) to a maximum of 220 ksi. The fracture toughness of such structures, however, reaches a minimum value of  $\sim 20 \text{ ksi}\sqrt{\text{in.}}$  when the omega particle size exceeds  $100 \text{ \AA}$  irrespective of aging temperature or aging time. The cracking plane of beta + omega structures is near  $\{100\}_{\beta}$ , and the fracture mode macroscopically resembles cleavage. On a microscopic scale, however, the "dimpled" fracture topography is more characteristic of a ductile mode of failure.

Beta + alpha structures show good combinations of yield strength and fracture toughness. Unfortunately the best combinations, e.g.,  $\sigma_Y = 153 \text{ ksi}$  and  $K_{Ic} = 66 \text{ ksi}\sqrt{\text{in.}}$  also exhibit the greatest susceptibility to stress-corrosion cracking in aqueous solutions containing halide ions, e.g.,  $K_{Isc} = 26 \text{ ksi}\sqrt{\text{in.}}$  Higher aging temperatures result in less susceptible conditions. In contrast to the stress-corrosion cracking of alpha + beta alloys, the fracture mode of Ti-11.5Mo-6Zr-5Sn in aqueous solutions is intergranular. As-quenched and beta + omega structures are immune to stress-corrosion cracking in neutral aqueous solutions.

## **Publications**

**"Stress Induced Transformations in Ti-Mo Alloys," J. A. Feeney and M. J. Blackburn, Boeing Document D6-25210, February 1970; to be published in Journal of the Institute of Metals, June 1970**

**"Effect of Microstructure on the Strength, Toughness, and Stress-Corrosion Cracking Susceptibility of a Metastable Beta Titanium Alloy (Ti-11.5Mo-6Zr-4.5Sn)," J. A. Feeney and M. J. Blackburn, Boeing Document D6-24472, February 1970; submitted to Metallurgical Transactions, May 1970**

## **Presentations**

**Presentation at Georgia Tech. , May 1968, entitled "Physical Metallurgy and Stress Corrosion Cracking of Beta Titanium Alloys."**

**Presentation at Stanford University, April 1968.**

**Presentation at University of Utah, February 1970.**

The Boeing Company

## THE MICROSTRUCTURAL, HEAT TREATMENT, AND MECHANICAL PROPERTY RELATIONSHIPS IN A BETA TITANIUM ALLOY

H. Narayanan (University of Washington, Seattle)

### Objective

The objectives of the investigation can be broadly classified into three phases: (a) obtain a complete understanding of the phase transformation characteristics of the all-beta alloy Ti-13V-11Cr-3Al (B120VCA), (b) obtain mechanical property data following selected heat treatments, (c) compare the information generated in (a) and (b) with Boeing stress-corrosion cracking data.

### Approach

The phase transformation characteristics were investigated using electron microscopy as the primary technique. X-ray diffraction, electrical resistivity measurements, and optical microscopy were also used. The mechanical property measurements include data for hardness, yield stress, ultimate tensile stress (UTS), and percent elongation for various heat treatments. The work-hardening characteristics of the alloy in the all-beta and the aged conditions have been examined.

### Achievements

#### a) Phase Transformations

1. The alloy undergoes a spontaneous transformation during thin foil preparation; the product is face cubic centered.
2. No omega phase forms during aging below 500°C.
3. The metastable beta decomposes into two body cubic centered (bcc) phases at aging temperatures below approximately 550°C, one phase rich in solute and the other phase lean in solute.
4. The solute rich phase, designated by the author as  $\beta_2$ , forms as disc-shaped particles parallel to (100) type planes of the matrix.
5. Prolonged aging in the above temperature range results in the formation of the equilibrium alpha phase at grain boundaries, at the interfaces between the two bcc phases, and at matrix-inclusion interfaces (when inclusions are present).
6. At aging temperatures below 500°C, the alpha phase appears as needle-like particles; a massive alpha is observed after aging above 500°C.
7. Deformation of the solution treated specimens prior to aging accelerates the formation of the alpha-phase.
8. The solution treatment temperature and the subsequent cooling rate have no apparent influence on the kinetics of alpha-phase precipitation.



9.  $\text{TiCr}_2$  does not appear after aging at  $400^\circ\text{C}$  for 2000 hours. The compound does form at shorter times at temperatures above  $500^\circ\text{C}$ .
10. The formation of  $\alpha$  and  $\text{TiCr}_2$  exhibits "C"-curve behavior with the "nose" of the TTT curve at about  $550^\circ\text{C}$ .
11.  $\alpha$  and  $\text{TiCr}_2$  appear as a lamellar structure at aging temperatures above  $500^\circ\text{C}$ .

#### b) Mechanical Properties

Variations in hardness (Rockwell C) have been measured as a function of aging time for various aging temperatures in the range  $300^\circ\text{C}$  to  $650^\circ\text{C}$ . The following observations were made:

1. The separation into two bcc phases yields no apparent increase in hardness.
2.  $\alpha$  is the primary age-hardening constituent; the size and distribution of this phase influences the observed hardness.
3. Overaging can be attributed to the precipitation of  $\text{TiCr}_2$ .

Tensile property measurements show a wide range of strengths and ductilities as a result of the various heat treatments. In the as-quenched condition the alloy is quite ductile and exhibits an elongation of approximately 25%. Furthermore, a very low work-hardening rate, which is not a function of strain rate, is observed.

With the precipitation of  $\alpha$ , the yield strength and the UTS increased while the percent elongation decreased. Maximum UTS values were obtained after aging for 1000 hours at  $350^\circ\text{C}$ ; however, these specimens failed with little or no yielding. The precipitation of  $\text{TiCr}_2$  prompted embrittlement.  $\alpha$ - $\beta$  specimens exhibit strain aging characteristics similar to those observed with low carbon steels.

#### Publications and Theses

"Decomposition of the Metastable Beta Phase in the All Beta Alloy Ti-13V-11Cr-3Al," G. Hari Narayanan and T. F. Archbold, accepted for publication by Trans. AIME pending revision

"Strain Aging of an All-Beta Titanium Alloy," G. Hari Narayanan and T. F. Archbold, submitted to Metallurgical Transactions

Mr. Narayanan's doctoral dissertation is expected in June 1970

The Boeing Company

## HYDROGEN EMBRITTLEMENT OF TITANIUM ALLOYS

A. K. Mukherjee (University of California, Davis)

### Abstract

The various mechanisms that have been put forward to explain stress-corrosion cracking are briefly summarized. The experimental observations of stress-corrosion cracking in titanium alloys in widely different environments are discussed. Evidence from the literature for and against the possibility that hydrogen plays a role in the stress-corrosion cracking of titanium alloys is documented. An experimental approach is outlined in an attempt to establish if environmental cracking of titanium alloys in specific environments can be attributed to a process similar to hydrogen embrittlement.

### Publications

"The Possible Role of Hydrogen in Stress-Corrosion Cracking of Titanium Alloys,"  
A. K. Mukherjee, Boeing Document No. D6-23621, September 1967 (DDC Accession  
No. AD 685378)

## The Boeing Company

## OXIDATION BEHAVIOR OF TITANIUM

A. K. Mukherjee (University of California, Davis)

## Background

Apart from the effect of enhanced oxidation of titanium in an oxidizing environment at an elevated temperature, oxygen has another important effect on titanium. Interstitially dissolved oxygen may exhibit ordering, and the tendency for this increases with greater oxygen content and decreasing temperature. Since interstitially dissolved oxygen acts in much the same way as aluminum, the ordering reaction between titanium and oxygen may render an alloy susceptible to stress-corrosion cracking, even though the aluminum content may be below the permissible amount.

## Approach

Because oxygen is the most prevalent medium for oxidation in titanium, all literature to date is concerned with oxidation in an oxygen environment. However, there is another important agent for oxidation of titanium—ozone. This agent is produced at a high altitude, due to bombardment of oxygen molecules by ultra-violet rays. The experimental information available in literature on the oxidation characteristics of pure titanium in an oxygen environment was summarized. Also included was a tentative outline for experiments that may be pursued in the preliminary stage of a comprehensive investigation to delineate the effect of ozone on the mechanical and structural properties of titanium alloys.

## Publication

"Oxidation Behavior of Titanium - A Review," A. K. Mukherjee, Boeing Document No. D6-23620, September 1967

## American University

**THE INFLUENCE OF SELECTED ANIONS AND CATIONS ON THE CORROSION OF ALUMINUM ALLOYS**

R. T. Foley, A.A. Adams\*, A. M. McKissick, Jr.\*, R. E. Meyers\*, and P. P. Trzaskoma\*

(\* Graduate Student)

**Objective**

To determine the effect, in a quantitative way, of certain anions and cations on the corrosion behavior of aluminum alloys type 7075 and 2024.

**Approach**

The results of conventional immersion tests are being coupled with the measurement of "scrape" potential and "scrape" potential decay of "clean" aluminum in the presence of anions. It is expected that chemical species that determine the corrosion rate will alter the rate of return to the steady state potential.

**Achievements**

It has been established that anions operate in a specific manner suggestive of chemical reaction rather than some physical adsorption process. Certain combinations of anions ( $\text{NO}_3^-$  and  $\text{Cl}^-$ ) produce a synergistic effect rather than an additive effect, increasing corrosion by an order of magnitude. The magnitude of the shift from the open circuit potential to the scrape potential is related to the corrosive character of the anions.

**Publications and Theses**

"The Role of Selected Ions in the Corrosion of Aluminum," R. E. Meyers, M. S. Thesis, June 1969

"The Effect of Anions on the Corrosion Resistance of High-Strength Aluminum Alloys," A. M. McKissick, Jr., M. S. Thesis, January 1970

"A Brief Communication on Synergistic Effects of Anions in the Corrosion of Aluminum Alloys," A. M. McKissick, Jr., A. A. Adams, and R. T. Foley, J. Electrochem. Soc. **117**, 1970, p. 1459

## American University

**THE INFLUENCE OF ANIONS ON THE ELECTROCHEMICAL KINETICS OF THE PITTING OF IRON AND ALUMINUM**

R. T. Foley and F. D. Bogar\*

(\*now with the Naval Research Laboratory)

**Objective**

To establish the role of anions in the pitting process of aluminum and iron.

**Approach**

The potentiokinetic technique of Engell and Stolica is being applied to establish the kinetics of pitting in various electrolytes, including the salt mixtures that give synergistic effects. These experiments are supplying the kinetic order of reaction and the apparent energy of activation.

**Achievements**

The kinetics of pitting is expressed in terms of an induction time,  $\tau$ . The electrode is held at some specific potential, either in the active or passive state, and at some induction time a sharp rise in current is observed. The temperature dependence of the induction time was measured over the range 15°-40°C and from the slope the apparent energy of activation was calculated to be 30 k cal/mole. This suggests that the anion participates in some sort of chemical reaction such as complex ion formation. Further experimentation has shown that there is a critical concentration of chloride ion for pitting inception.

**Publications and Thesis**

"Role of Chloride Ion in Iron Corrosion," R. T. Foley, *Corrosion* **26**:2, Feb 1970, pp. 58-70

"The Influence of Anions on the Kinetics of the Pitting of Iron and Aluminum," F. D. Bogar, Ph.D. Thesis, October 1970

"The Influence of Chloride and Sulfate Ions on the Corrosion of Iron in Sulfuric Acid," S. E. Trautenberg and R. T. Foley, *J. Electrochem. Soc.* **118**:7, 1971, pp. 1066-1070

American University

## RELATIONSHIP BETWEEN COMPLEX ION FORMATION AND STRESS CRACKING OF HIGH STRENGTH ALLOYS

R. T. Foley, and B. J. Alexander\*

(\* Graduate Student)

### Objective

To establish the relationship between the formation of complex ions and the stress cracking of alloys in specific environments.

### Approach

A review of published reports dealing with chemical reactions occurring during the stress-corrosion process is being made. Based on these findings electro-chemical-optical experiments will be designed to measure the appearance of complex ions under conditions similar to those encountered in stress-corrosion cracking.

### Achievements

It is apparent that with specific alloy systems and specific environments, e.g., copper alloys in ammonia atmospheres, stress cracking proceeds with complex ion formation. However, at this stage it is not possible to make generalizations covering all alloy systems.

## Carnegie-Mellon University

**EFFECT OF WATER ON CRACK PROPAGATION IN MAGNESIUM OXIDE SINGLE CRYSTALS**

G. W. Groves\*, A. Kelly†, and D. A. Shockey‡

(\* now at University of Oxford, England)

(† Visiting Professor)

(‡ Graduate Student)

**Objective**

To measure the apparent surface energy of fractured MgO in air and water, and to examine the effects of a polar fluid on crack mechanics.

**Approach**

Small, double cantilever beam specimens were fashioned from large monocrystals of MgO by cleavage and were tested in such a way that the crack advanced in a series of propagations, each of which yielded a value of the apparent surface energy of the fracture surface. The specimen environment was changed after a small number of propagations, and the values of apparent surface energy obtained on the same specimen in the different environments were compared.

**Achievements**

The apparent surface energy for crack propagation in air was found to be approximately 1700 ergs/cm<sup>2</sup> while that in water was about 4000 ergs/cm<sup>2</sup>. While the fracture surface in air was relatively smooth, in water it became very rough. It was concluded that the energy absorbed in forming steps on the fractured surface could in principle account for the increase in apparent surface energy. Once the rough surface was initiated in water it would continue to propagate in air.

**Publications and Theses**

"Origin of Water-Induced Toughening in MgO Crystals," D. A. Shockey and G. W. Groves, J. Am. Ceramic Soc. 52: 2, 1969, p. 82

"Effect of Water on Toughness in MgO Crystals," D. A. Shockey and G. W. Groves, " J. Am. Ceramic Soc. 51: 6, 1968, p. 299

"Effect of Water on Toughness in MgO Crystals" Ph.D. Thesis, D. A. Shockey, 1968

**Presentations**

AIME Meeting, February 1967, Los Angeles, California

ARPA Meeting, May 1967, Carnegie-Mellon University

Pratt and Whitney Research Labs, February 1968, Middletown, Connecticut

Seminar presented to the Abteilung für Festkörpermechanik, September 1968,  
Ernst-Mech-Institut, Freiburg, Germany

British Ceramic Society-Basic Science Division Meeting on the Mechanical  
Properties of Ceramics, December 1968, Royal Aeronautical Society, London,  
England



## Carnegie-Mellon University

## THE RATE OF ANODIC POLARIZATION OF IRON AND IRON ALLOYS

Paul Fugassi and A. Tirman\*

(\* Graduate Student)

## Objective

To measure the kinetics of anodic polarization and depolarization of Armco iron and various iron alloys such as AISI 4340 and AISI 4140.

## Approach

A galvanostatic method was used with the changes in EMF, resulting from changes in current, being measured on a recorder. With interruption of the current, a depolarization voltage curve was also obtained. The electrolytes employed were saturated aqueous solutions of  $\text{FeCl}_2$ ,  $\text{FeSO}_4$ , etc. The purpose of using saturated solutions was to minimize concentration polarization.

## Achievements

Measurements have been made mainly on Armco iron. Improvement in the experimental method is necessary as the present precision is not too high. Empirical equations have been developed for the rates of anodic polarization and depolarization, but the spread in the experimental constants must be decreased before satisfactory conclusions can be made as to the nature of the mechanisms involved.

## Thesis

"The Rate of Anodic Polarization of Iron and Iron Alloys," A. Tirman, Ph.D. Thesis, August 1960

Carnegie-Mellon University

## KINETICS OF PHASE TRANSFORMATIONS IN HIGH PURITY BINARY TI-AL ALLOYS

H. W. Paxton, P. A. Flinn, and T. E. O'Connell\*

(\* Graduate Student)

### Objective

All useful titanium alloys contain several percent of aluminum, and the ordering reaction plays a significant role in providing strength and in contributing to brittleness. The kinetics of coarsening of ordered domains is poorly understood; the objective of this study is to obtain quantitative data on this phenomenon in high purity alloys near the composition  $Ti_3Al$ .

### Approach

High purity alloys prepared by levitation melting are being studied by transmission electron microscopy and X-ray diffraction analysis. The X-ray technique involves measuring the width of superlattice reflections and comparing them with fundamental peaks to obtain an average domain size.

### Achievements

Some splat samples were prepared from master alloy rods of high purity and some from oxygen contaminated rods. The splat samples quenched from the melt at  $10^4$  degC/sec were found by X-ray diffraction to be ordered in the case of contaminated samples, while the pure samples were disordered.

A disordered sample was heated to  $512^\circ\text{C}$  for times ranging from 0.25 hr to 100 hr. For all conditions the  $(101)_{\alpha_2}$  reflection was narrow, but the diffracted intensity associated with the peak increased with time. The continuous peak width suggests a heterogeneous growth mode in which entire  $\alpha$  grains are ordered at once while the rest of the grains remain disordered. Fifty percent transformation occurred after two hours.

### Thesis

Thesis to be written in late 1971.

## Carnegie-Mellon University

**INFLUENCE OF SURFACE FILMS ON THE STRESS-CORROSION CRACKING SUSCEPTIBILITY OF TITANIUM AND TITANIUM ALLOYS**

A. M. Guzman

**Objective**

To study the effect of oxide films on the initial stages of stress-corrosion cracking, since such films are a prominent feature of some theories of such cracking.

**Approach**

Tests on the adhesion of oxide layers with titanium-based substrates by means of torsional recovery experiments of twisted wires were carried out. Tests to determine the time to failure of U-bend "coated" and "uncoated" specimens in methanol-bromine and methanol-iodine solutions were also performed. Light microscopy was used to observe the specimen surface. The fracture surface was studied with the scanning electron microscope.

**Achievements**

It has been shown that the Barrett abnormal after-effect is present in wires coated with an anodic oxide layer. It was concluded that this layer is adherent to the substrate and is a good barrier to the motion of dislocations. Ti-5Al-2.5Sn U-bend specimens coated with an anodic oxide layer failed in shorter times than the uncoated samples when exposed to methanol-iodine solutions. A possible explanation of the observed effect is given in terms of the influence of the coating of the deformation mode of the substrate. The coating acts as a barrier to the motion of dislocations and creates pile-ups in the vicinity of the interface oxide-substrate. Cracking of the surface layer may result as a consequence of these pile-ups. It is proposed that any subsequent deformation of the substrate will be confined to those regions where the oxide cracked. Therefore, high slip steps may be formed in the coated samples but not in the uncoated specimens where the deformation is more uniform. It is suggested that the higher susceptibility of the coated specimens with respect to the uncoated is directly related to the repassivation of the high freshly formed slip steps.

## Carnegie-Mellon University

## INTERGRANULAR FRACTURE IN AN Al-15 wt-% Zn ALLOY

J. R. Low, Jr., and W. J. Kovacs\*

(\* Graduate Student)

## Objective

The cracking kinetics of an Al-15 wt-% Zn alloy as a function of both microstructure and environment have been investigated.

## Approach

The kinetics of intergranular crack propagation have been studied by measuring the elastic energy released during the cracking of double cantilever beam specimens. A series of microstructures containing differing volume fractions of G. P. zones and  $\alpha'$  were tested both in air and in a 0.5 molar NaCl solution. During the course of this investigation, specimens of both the polycrystalline and bicrystalline types were employed.

## Achievements

The results of this work indicate that, for the microstructures studied, crack velocities in the NaCl solution were an order of magnitude higher than those in air when tested at the same stress intensity level. This work also showed that the microstructure controlled the cracking process through the effect of microstructure on the deformation process. Specimens which were strengthened by large G. P. zones exhibited coarse slip characteristics and proved to crack very rapidly, while specimens hardened by small G. P. zones exhibited fine slip and cracked relatively slowly. The work performed on bicrystals revealed that when slip could be transferred across the grain boundary cracking was slow, but when slip transfer was impeded by the boundary cracking was rapid.

## Thesis and Publication

"Intergranular Fracture in an Al-15 w/o Zn Alloy," W. J. Kovacs, Ph.D. Thesis, 1969

"Intergranular Fracture in an Al-15 wt-% Zn Alloy," William J. Kovacs and John R. Low, Jr., submitted to TMS-AIME

## Carnegie-Mellon University

THE EFFECT OF MICROSTRUCTURE ON THE STRESS-CORROSION  
SUSCEPTIBILITY OF AN Al-Zn-Mg ALLOY

R. D. Townsend\* and A. J. DeArdo, Jr.†

(\* now at CEGB Laboratories, Leatherhead, Surrey, England)  
(† Graduate Student)

## Objective

The purpose of this work was to determine how the microstructure controls the stress-corrosion susceptibility (SCS) of an Al-7 wt-% Zn-2.3 wt-% Mg alloy.

## Approach

Heat treatments were developed that generated a series of microstructures in which the precipitate free zone (PFZ) and matrix precipitate were varied under controlled conditions. Smooth sheet tensile specimens were heat treated to these microstructures and tested for susceptibility to stress corrosion in a 3.5 wt-% NaCl solution under both constant-load and constant-deflection conditions. Since there was a strong correlation between the type, size, and spacing of the matrix precipitate and SCS, a deformation study was conducted to determine how the matrix precipitate controls the deformation process and thereby influences SCS.

## Achievements

The results of this work show that SCS is controlled by the type, size, and spacing of the matrix precipitate. Neither the presence nor the width of the PFZ had any effect on SCS. In certain cases, the grain boundary precipitate appeared to influence SCS. The matrix precipitate appears to control SCS through its effect on the deformation accompanying a stress-corrosion crack. Specimens which exhibited straight, intense slip bands proved to be very susceptible to stress-corrosion cracking while specimens which showed weak, wavy slip bands had a lower SCS. This behavior is explained in terms of the dislocation-matrix precipitate interaction and its influence on slip band-grain boundary intersections.

## Publication and Thesis

"Effect of Microstructure on the Stress-Corrosion Susceptibility of an Al-Zn-Mg Alloy," A. J. DeArdo, Jr., Ph.D. Thesis, 1969

"Effect of Microstructure on the Stress-Corrosion Susceptibility of an Al-Zn-Mg Alloy in a NaCl Solution," A. J. DeArdo, Jr., and R. D. Townsend, Metallurgical Transactions 1, Sept 1970, pp. 2573-2581

## Presentations

Spring Meeting of TMS-AIME, Pittsburgh, Pa., May 1969  
ALCOA Research Laboratories, New Kensington, Pa., Feb 1970  
Westinghouse Research Laboratories, Pittsburgh, Pa., April 1970

Carnegie-Mellon University

## STRESS-CORROSION CRACKING OF ALUMINUM 7075-T651 ALLOY IN ORGANIC LIQUIDS

H. W. Paxton and R. P. M. Procter\*

(\* The University of Manchester, Manchester, England)

### Objective

To determine under what conditions aluminum alloy 7075-T651 might be susceptible to stress-corrosion cracking in organic environments, and to attempt to identify the mechanism(s) of cracking.

### Approach

Cantilever beam specimens of commercial 7075-T651 (representing a typical, moderately susceptible, high strength aluminum alloy) containing a fatigue precrack normal to the elongated grains were exposed to fresh dry reagent-grade methanol, ethanol, ethylene glycol, and isopropanol. Measurements were made on average crack velocity and the fracture path and appearance were studied.

### Achievements

It has been shown that stress-corrosion cracks will propagate from a fatigue precrack in 7075-T651 aluminum alloy exposed to various organic environments; stress-corrosion cracks, however, did not initiate in smooth specimens. Evidence is presented which indicates that the crack propagation probably is not due to traces of water absorbed in the oxide film at the crack tip, or in the environments. The stress-corrosion crack growth rate has been measured in ethanol and carbon tetrachloride as a function of the plane-strain stress-intensity factor  $K_I$ . A linearly increasing relationship has been observed, and, from these results, values of  $K_{I_{SCC}}$  for each environment have been estimated. The results of a fractographic analysis of the fracture surfaces are described. Evidence is presented to show that some limited dissolution of aluminum in the environments occurs, and it is suggested that, as with aqueous stress corrosion of aluminum alloys, an electrochemical reaction is involved in the cracking.

### Publications

"Stress-Corrosion Cracking of Aluminum Alloy 7075-T651 in Organic Liquids," published in Journal of Materials, JMLSA 4, 1969, p. 729

### Presentations

ASTM Symposium on Stress-Corrosion Cracking, Atlanta, Ga., Sept. 1968

Fall Meeting of TMS of AIME, Detroit, Michigan, October 1968

## Carnegie-Mellon University

## THE EFFECT OF PRIOR-AUSTENITE GRAIN SIZE ON THE STRESS-CORROSION SUSCEPTIBILITY OF AISI 4340 STEEL

H. W. Paxton and R. P. M. Procter\*

(\* The University of Manchester, Manchester, England)

## Objective

To determine whether the strength and the stress-corrosion resistance of AISI 4340 steel could be simultaneously improved by the development of ultrafine prior-austenite grain sizes.

## Approach

Ultrafine grain sizes were produced in AISI 4340 by repeated low-temperature austenitizing and oil quenching. The conventional mechanical properties, fracture toughness, and stress-corrosion behavior in 3 1/2% Na Cl solution were measured as a function of grain size. Fractographic and metallographic examinations of the failure surfaces were carried out.

## Achievements

Using both conventional and non-conventional austenitizing heat treatments, four prior-austenite grain sizes covering the range ASTM 6-11 have been developed in a vacuum-degassed aircraft quality AISI 4340 steel; these alloys were subsequently oil-quenched and tempered 1 hr. + 1 hr. at 400° F. Hardness data show that the yield strength of these steels increases with decreasing prior-austenite grain size, over the range 220-260 ksi. The prior-austenite grain size does not affect the  $K_{Isc}$  values (all lie within the range 15-17 ksi  $\sqrt{\text{in.}}$ ), but decreasing the prior-austenite grain size decreases somewhat the rate of stress-corrosion crack propagation (i. e., the initial stress intensity vs. time-to-failure curves are shifted increasingly to the right, toward longer failure times, at a given  $K_{Ic}$  value, with decreasing prior-austenite grain size). Fractographic studies show propagation along prior austenite grain boundaries with little plastic deformation visible.

## Publications and Theses

"The Effect of Prior-Austenite Grain-Size on the Stress-Corrosion Susceptibility of A. I. S. I. 4340 Steel," published in ASM Trans. Quart. 62, 1969, p. 989

## Presentations

Cebelcor Corrosion Conference, Brussels, Belgium, September 1969

## Carnegie-Mellon University

**THE DIFFUSION OF HYDROGEN IN IRON AND STEELS AROUND ROOM TEMPERATURE**

P. G. Shewmon\* and J. Y. Choi

(\*now Director, Metallurgy Division, Argonne National Laboratory)

**Objective**

Because of the importance of hydrogen in stress-corrosion cracking, it is necessary to have reliable data on its permeability and diffusivity in iron and steel near room temperature.

**Approach**

The transport of hydrogen through a diaphragm made from various ferrous materials, and in contact on one side with aqueous solutions, was monitored by a mass spectrometer. Both steady state and transient conditions were examined, and the role of trapping sites was evaluated.

**Achievements**

Values of permeability and diffusivity in fully annealed and cold worked "pure iron" have been obtained between 10° and 100° C. Some annealed steels with carbon contents up to 1.46% were also examined from the point of view of carbides as "traps." Permeability is very sensitive to environment and surface preparation so a single value cannot be quoted meaningfully; the value of the diffusion coefficient in fully annealed iron is

$$D = 2.2 \times 10^{-3} \exp \left\{ - \frac{3100}{RT} \right\} \text{ cm}^2/\text{sec.}$$

between 10° and 100° C. Cold working results in lower values of D and higher values of Q. It was not possible to extend the work to quenched-and-tempered steels, but this is well worth doing.

**Publications and Theses**

J. Y. Choi, "Diffusion of Hydrogen in Iron," Met. Trans. 1, 1970, p. 911

**Presentations**

Fall Meeting of TMS of AIME, Detroit, Michigan, October 1968



## Carnegie-Mellon University

**THE EFFECT OF IMPURITIES ON THE STRESS-CORROSION SUSCEPTIBILITY OF Ni (300 Grade) MARAGING STEEL**

H. W. Paxton and R. P. M. Procter\*

(\* The University of Manchester, Manchester, England)

**Objective**

To determine the effect of commercially present impurities on the stress-corrosion cracking susceptibility of 18 Ni (300 grade) maraging steels.

**Approach**

A series of laboratory heats of 18 Ni (300 grade) maraging steels of overall commercial purity but containing also deliberate impurity additions of sulphur, phosphorus, carbon, chromium, and silicon + manganese has been studied. The fracture toughness and stress-corrosion resistance (determined using plane strain fatigue-precracked specimens tested in 3.5% sodium chloride solution) of these steels have been compared to the fracture toughness and stress-corrosion resistance of a commercial purity 18 Ni (300 grade) maraging steel with no deliberate impurity additions, and to a similar steel prepared from special high purity melting stock.

**Achievements**

The most important conclusions reached are that: (1) Ultrahigh purity steels do not have significantly improved stress-corrosion resistance but do show useful increases in fracture toughness when the carbon content is less than 0.005%; (2) Simultaneous additions of 0.15% Mn + 0.15% Si result in extremely low fracture toughness values; (3) High carbon contents (greater than 0.03%) result in marginally improved stress-corrosion resistance; (4) Cr contents of 0.30% result in rather poor stress-corrosion properties. These results have been correlated with the electron transmission microstructure of the steels and the results of a fractographic analysis of the fracture surfaces. The tougher steels have larger "dimple sizes", due presumably to a smaller number of nucleation sites for this ductile failure mechanism.  $K_{Isc}$  in all cases is disappointingly low, and improvement by the compositional variations studied is marginal at best.

**Publications and Theses**

"The Effect of Trace Impurities on the Stress-Corrosion Susceptibility and Fracture Toughness of 18 Ni (300 Grade) Maraging Steel," to be submitted for publication

**Presentations**

Spring Meeting of TMS of AIME, Las Vegas, Nevada, May 1970

## Carnegie-Mellon University

## STUDIES OF THE STRESS-CORROSION BEHAVIOR OF 18 Ni (300 Grade) MARAGING STEEL

H. W. Paxton and A. J. Stavros\*

(\*Graduate Student)

## Objective

To investigate the roles of microstructure and electrochemistry in the stress-corrosion cracking of a (300 grade) maraging steel in an attempt to understand the mechanism(s) of cracking.

## Approach

Pre-cracked cantilever beams were tested in plane strain in 3% Na Cl solution, in  $H_2SO_4$  and distilled water after heat treatments designed to vary precipitate size, amount of retained austenite, and austenite grain size. Polarization curves for anodic and cathodic reactions were obtained, and cracking was then studied as a function of potential and pH.

## Achievements

$K_{Isc}$  was insensitive to any of the variables studied. Crack growth rates did vary (~ two orders of magnitude) but this is not enough to be of practical significance. The cracks branched in fine-grained austenite (ASTM 9) whenever  $K_I$  was greater than about 31 ksi  $\sqrt{in}$ , but not in coarse-grained austenite (ASTM 0). The cracks were invariably along prior austenite grain boundaries; a detailed examination of fracture surfaces did not permit comments on mechanism(s) of cracking. The results are all consistent with hydrogen being generated at the crack tip entering the metal and embrittling it.

## Publications and Theses

A. J. Stavros, "Stress Corrosion Cracking Behavior of an 18% Ni Maraging Steel," Ph.D. thesis, Carnegie-Mellon, August 1969

A. J. Stavros and H. W. Paxton, "Stress-Corrosion Cracking Behavior of an 18% Ni Maraging Steel," submitted to Met. Trans., 1970

A. J. Stavros, "Effect of Heat Treatment on Anodic Polarization of an 18% Ni Maraging Steel," to be submitted to Corrosion Science

## Presentations

Spring Meeting of TMS of AIME, Las Vegas, Nevada, May 1970

## Carnegie-Mellon University

## ELECTRON MICROSCOPE INVESTIGATION OF STRESS CORROSION IN 12 Ni MARAGING STEELS

W. M. Leo

## Objective

To evaluate the microstructures obtained in 12 Ni maraging steel after different aging treatments and to determine the stress-corrosion behavior in 3.5 Na Cl as the microstructure is changed.

## Approach

This alloy was aged at 800, 900, and 1000° F, and the microstructures obtained as a function of time and temperature were studied using the electron microscope. Self-stressed double cantilever beam (DCB) specimens were used to evaluate the stress-corrosion susceptibility as a function of microstructure. The initial stress intensity level used was 100 ksi  $\sqrt{\text{in}}$ .

## Achievements

In contrast to 18 Ni maraging steels it appeared that the main hardening precipitate was not  $\text{Ni}_3\text{Mo}$  but either  $\text{Ni}_3\text{Ti}$  or  $\text{Fe}_2\text{Ti}$ , which are hexagonal. The orientation relationship was found to be  $(0001) \text{Ni}_3\text{Ti}$  or  $\text{Fe}_2\text{Ti} // (110)_\alpha \text{Fe}$ . The lath boundaries and dislocations appeared to be preferential sites for precipitation rather than the prior austenite grain boundaries. The stress-corrosion behavior of the 12Ni-5Cr-3Mo alloy could not be determined due to transgranular crack propagation out of the initial plane in the DCB specimens.

## Carnegie-Mellon University

**EFFECT OF THE SPECIMEN ORIENTATION WITH RESPECT TO THE ROLLING DIRECTION ON THE MECHANICAL PROPERTIES AND STRESS-CORROSION CRACKING SUSCEPTIBILITY OF Ti-5Al-2.5Sn SHEETS**

A. M. Guzman

**Objective**

To study the effect of the microstructural and textural changes introduced by the rolling process on the stress-corrosion cracking (SCC) behavior of Ti-5Al-2.5Sn in methanol-iodine environments.

**Approach**

Smooth U-bend specimens were stressed (initially very close to the yield point) at various angles relative to the rolling direction in methanol-iodine solutions. The eventual fracture surface was examined with the scanning electron microscope and replicas. Texture was studied using the X-ray back reflection technique. Light and transmission electron microscopy were used to observe the microstructure. Stress-strain curves were obtained on a hard tensile machine to study yielding phenomena.

**Achievements**

The experiment demonstrates that a high (SCC) susceptibility is associated with the transverse direction. Studies of the tensile properties of the material show that a yield point phenomenon is present in the transverse specimens but not in the longitudinal samples. The crystallographic texture indicates that the poles of the basal plane are tilted toward the transverse direction, and thin foil transmission electron microscopy observations show that twinning is predominant when the stress is in this direction. Deformation twinning and its subsequent effects were proposed to explain the presence of the observed yield point phenomenon. Also, twinning may provide a mechanism for rapid crack nucleation in the transverse specimens which can account for their high SCC susceptibility in a methanol-iodine solution.

**Publications and Theses**

"Anisotropic Yielding Behavior of Ti-5Al-2.5Sn," to be submitted to Metallurgical Transactions.

"Influence of the Specimen Orientation on the Stress-Corrosion Cracking Susceptibility of Ti-5Al-2.5Sn Sheet in Methanol-Iodine Environment" to be submitted.

## Carnegie-Mellon University

**THE EFFECT OF VACANCY CONCENTRATION ON THE KINETICS OF PRECIPITATION  
IN AN Al-Zn-Mg ALLOY**

R. D. Townsend\*, R. A. Osiecki<sup>†</sup>, and R. P. Hunt

(\* now at CEGB Research Laboratories, Leatherhead, Surrey, England)

(† Undergraduate Student)

**Objective**

The kinetics of G. P. zone formation as a function of vacancy concentration have been investigated.

**Approach**

The hardness response to aging of an Al-7 wt-% Zn-1.0 wt-% Mg alloy has been determined for various aging temperatures below the G. P. zone solvus. This response was determined for specimens quenched under various conditions. Incubation times were measured from these aging curves and transformation curves were constructed.

**Achievements**

The results of this work show that the kinetics of G. P. zone formation appear to be independent of vacancy concentration when aging was performed below the nose of the transformation curve. The kinetics of G. P. zone formation appear to be strongly influenced by the vacancy concentration when aging was performed above the nose of the transformation curve.

**Presentations**

Spring Meeting of TMS of AIME, Pittsburgh, Pa., May 1969

Carnegie-Mellon University

## THE EFFECT OF MACHINING AND GRINDING ON THE STRESS-CORROSION SUSCEPTIBILITY OF METALS AND ALLOYS

H. W. Paxton and R. P. M. Procter\*

(\* The University of Manchester, Manchester, England)

### Objective

To survey and review the relevant literature on the effects of machining and grinding on the stress corrosion of metals and alloys, and to report thereon, because of the potential importance of surface preparation techniques on eventual cracking.

### Approach

A comprehensive literature survey was undertaken to review published data on the effect of machining and grinding on the stress-corrosion susceptibility of various alloys. On the basis of this, a review paper was prepared and presented as paper no. EM68-520 at the ASTM Symposium on Surface Integrity held in Pittsburgh on 24-25 January 1968.

### Achievements

The abstract of the above paper is given below as being more appropriate than the customary "Achievements."

"A general but necessarily brief introductory review of the occurrence, phenomenology and mechanistic theories of stress-corrosion cracking (in the widest sense of the words) in metals and alloys is provided. Those changes which are produced in the surface layers of metals by machining and grinding operations, and which could conceivably affect the stress-corrosion susceptibility are discussed. A review of the rather scant published data on the experimentally observed effects of machining and grinding on the stress-corrosion performance of the major alloy systems (brasses, low carbon steels, high-strength alloy steels, stainless steels, aluminum alloys and titanium alloys) is presented. The implications of these results as far as stress-corrosion testing and performance is concerned are considered. Finally, some suggestions are made as to the most profitable avenues for future research."

### Publications and Theses

"The Effect of Machining and Grinding on the Stress-Corrosion Susceptibility of Metals and Alloys," published as ASTM paper EM68-520

### Presentations

ASTM Symposium on Surface Integrity, Pittsburgh, Pa., January 1968

## Carnegie-Mellon University

## THE NUCLEATION OF REVERTED AUSTENITE IN 18% Ni MARAGING STEELS

H. W. Paxton and H. L. Patts\*

(\* Graduate Student)

## Objective

To determine the primary nucleation site for reverted austenite in an 18% Ni maraging steel.

## Approach

At-temperature electrical resistivity and  $dR/dt$  measurements are employed to determine the mechanism of austenite reversion. Transmission electron microscopy, differential thermal analysis, and hardness measurements are being used to supplement the resistivity work.

## Achievements

A ternary (Fe-Ni-Mo) and a quaternary (Fe-Ni-Co-Mo) alloy have been melted and heat treated. At-temperature resistivity profiles and hardness curves have been compiled for the quaternary alloy at eight different aging temperatures between 700°F and 1000°F.

The susceptibility of various microstructures to austenite reversion has been investigated in the quaternary (Fe-Ni-Mo-Co) maraging alloy. Differential heat-treatments, designed to produce a constant volume fraction of precipitate, have been developed and are being employed to generate data which demonstrate the heterogeneous nucleation site for reverted austenite.

It has been found that the reversion kinetics are, as expected, closely related to the size, distribution, and the nature of the precipitate. Observations (by electron microscopy) of the unaged and reverted alloys are being conducted to confirm the conclusions drawn from the resistivity,  $dR/dT$  measurements, and hardness data.

The effect of cold work (approximately 50%) on the kinetics of the precipitation reaction and the reversion process has been considered. The conclusion to be drawn is that cold work produces no noticeable effect on these reactions for aging treatments in the range 650°F to 950°F. The precipitate  $Ni_3Mo$  appears to be the primary site for austenite reversion.

## Publications and Theses

"The Nucleation of Reverted Austenite in 18% Ni Maraging Steels", H. L. Patts, Ph.D. Thesis, July 1970

## Carnegie-Mellon University

**THE STRENGTH OF ALUMINUM 6wt-% ZINC 2 wt-% MAGNESIUM ALLOY SINGLE CRYSTALS**

C. D. Statham

**Objective**

To investigate the mechanical properties of these crystals as a function of aging time at 135° C.

**Approach**

The precipitate morphology as a function of aging time was examined in the electron microscope. These observations were correlated with the tensile yield strengths and slip line distribution. The temperature dependence of the yield stress and the rate theory parameters were also investigated for two different microstructures.

**Achievements**

The six different precipitate-matrix orientation relationships previously observed in fully overaged specimens were found to exist in only slightly overaged material. Strain field contrast suggested that precipitates of types 1-4 possessed a coherent interface around the rim of the plate. Precipitates of types 5 and 6 appeared to be completely incoherent at a very early stage in the aging curve. Examination of the slip traces produced by the movement of screw dislocations revealed that as aging proceeds cross slip becomes more difficult. At peak strength completely lamellar slip lines were observed on all faces of the specimen. The slip lines, rate theory parameters, and electron microscopy suggest that the dislocations cut the precipitates even in the overaged condition. The high hardening rates observed in the overaged condition must therefore be explained by the production of interface dislocations. Bamboo crystals in which the slip bands did not intersect the grain boundaries behaved in a similar way to the single crystals. However, if the slip bands did intersect the grain boundaries, then grain boundary cracking usually occurred especially in underaged crystals. The single crystals did not stress corrode.

**Publications**

C. D. Statham, "The Strength of Al-6 w/o Zn-2 w/o Mg Alloy Single Crystals," to be submitted for publication



## Carnegie-Mellon University

## DISLOCATION ARRANGEMENTS IN Al 6 wt-% Zn 2 wt-% Mg ALLOY SINGLE CRYSTALS

C. D. Statham

## Objective

To study the variation of the dislocation arrangements in this alloy as a function of strain and aging time below the G. P. zone solvus temperature.

## Approach

Single crystals were solutionized at 465° C, water quenched and aged at 135° C for various times. They were then deformed at room temperature, and thin sections were cut parallel to the primary slip plane and perpendicular to the primary Burgers vector. These sections were thinned and examined in a Philips E. M. 200 using a double tilt stage.

## Achievements

In the as-quenched material, the primary glide loops are elongated in the direction of the primary Burgers vector. With increasing strain these glide loops intersect to produce a structure consisting of loosely bundled edge dipoles and long screw dislocations. This type of arrangement is also observed in alloys containing G. P. zones although as aging proceeds the dipoles tend to become longer and less bundled together. There is evidence of planar arrangements in material containing G. P. zones. When  $\eta$  or  $\eta'$  precipitate just begins to form, the primary glide loops have very irregular shapes. At peak strength when the precipitates are several hundred Angstroms in size, the dislocation arrangements depend strongly on the details of the local precipitate-dislocation interaction. The dislocations appear to be able to pass through both the  $\eta$  and  $\eta'$  phases even in the overaged condition. The formation of interface dislocations and stacking faults, however, leads to a high work-hardening rate.

## Publications

C. D. Statham, "Dislocation Arrangements in Al-6 w/o Zn-2 w/o Mg Alloy Single Crystals," to be submitted for publication

## Carnegie-Mellon University

## THEORETICAL STUDY OF TRANSPORT PHENOMENA AT THE CRACK TIP

J. Swedlow and R. R. Shuck\*

(\* Graduate Student)

## Objective

Development of a quantitative technique for the solution of the electrochemical transport equations during stress-corrosion cracking.

## Approach

A computer program has been developed for solving electrochemical transport equations. This program will generate the time-dependent solution to the electrochemical transport equations for a two-dimensional crack-like region of elliptic, hyperbolic, or wedge shape. Ion transport by diffusion, migration, and convection is included. The program accepts as input crack geometry, crack opening rate, and the physical properties of the ionic species. The output may be varied depending on the requirements of a particular problem but includes, as a minimum, solvent velocity and ion concentrations as functions of time and two spatial variables.

## Achievements

The program is now being used to study crack initiation and the early stages of crack growth in a material modeled after the titanium base alloys. The model predicts that the aspect ratio of the crack dominates all other parameters (electrochemical or mechanical).

## Thesis

Ph.D. Thesis - R. R. Shuck (completed).

## Carnegie-Mellon University

## RATE OF SCC OF AISI 4340 STEEL FOIL

Paul Fugassi, E. G. Haney\*, and A. Tirman†

(\* Mellon Institute)

(† Graduate Student)

## Objective

To study the effect of various environments on the rate of stress-corrosion cracking of AISI 4340 steel foil.

## Approach

Samples were pre-treated in various solutions for definite time periods to:

1. Sulfide the surface, or
2. Adsorb on the surface oxides suitable organic dye-stuffs (hydrogen absorbers).

Following such treatments, the samples were immersed in 0.6M aqueous NaCl acidified to pH 1.5 with hydrochloric acid and the time to failure noted at 80% yield stress. The time to failure under stress was measured for untreated foil samples in which the corroding electrolytes were dilute solutions of heavy metal ions acidified to pH 1.5 with hydrochloric acid.

## Achievements

1. Sulfiding the surface of AISI 4340 foil increases the susceptibility to SCC.
2. Adsorption of dye-stuffs based on anthraquinone greatly decreases the susceptibility of AISI 4340 foil to SCC.
3. Quite dilute solutions of  $Pb^{++}$ ,  $Cd^{++}$ , and  $Sn^{++}$  greatly inhibit the SCC of AISI 4340 steel foil.

The results of this work indicate that hydrogen embrittlement is the major factor governing the cracking process.

## Publications and Theses

"The Rate of Anodic Polarization of Iron and Iron Alloys," A. Tirman, Ph.D. Thesis, August, 1969

"Environmental Effects of Sulfur and Sulfur Compounds on the Resistance to Stress-Corrosion Cracking of AISI 4340 Steel in Aqueous Chloride Solutions," A. Tirman, E. G. Haney, and Paul Fugassi, Corrosion 25, August 1969, pp. 342-344

"Environmental Effects of Anthraquinone Derivatives on the Resistance to Stress-Corrosion Cracking of AISI 4340 Steel in Aqueous Chloride Solutions," A. Tirman, Paul Fugassi, and E. G. Haney, Corrosion 25, October 1969, pp. 434-437

"Effect of Heavy Metal Ions on Susceptibility of AISI 4340 Foil to Stress-Corrosion Cracking in Dilute Aqueous HCl Solution," Paul Fugassi and E. G. Haney, *Corrosion* 26, March 1970, pp. 118-120

#### **Presentations**

"Effect of Heavy Metal Ions on SCC of AISI 4340 Steel Foil," Paul Fugassi and E. G. Haney, *ORPA Meeting (Steels)*, Carnegie-Mellon University, January 1970

## Carnegie-Mellon University

**MEASUREMENTS OF HYDROGEN OVERVOLTAGE ON VARIOUS SULFIDE ELECTRODES**

Paul Fugassi and Inam Khokhar

**Objective**

To measure hydrogen overvoltage on various sulfide electrodes in 0.6M NaCl at pH values of 2 and 6.5 in nitrogen and oxygen atmospheres.

**Approach**

A metal electrode, an electrode of the same metal previously sulfided, and a Ag/AgCl electrode are immersed in 0.6 M NaCl with provision for having an atmosphere of first tank nitrogen followed by an atmosphere of tank oxygen. The E.M.F. values of the Me and  $\text{Me}_x\text{S}_y$  electrodes against the reference Ag/AgCl electrode are measured over a period of time, first with  $\text{N}_2$  flowing through the cell and then with  $\text{O}_2$  flowing through the cell.

The metals used were: AISI 4340, annealed; AISI 4340, hardened; Pb, Sn, Mo and Fe.

**Achievements**

At pH values of 2 and 6.5, the cell involving Me and  $\text{Me}_x\text{S}_y$  electrodes had for all metals, except Fe and AISI 4340, the sulfide electrode as the cathode in both  $\text{N}_2$  and  $\text{O}_2$  atmospheres. Because of solution of FeS, the Fe-FeS system could only be investigated at pH 6.5. In an  $\text{N}_2$  atmosphere FeS is the cathode at pH 6.5, but in an oxygen atmosphere FeS is the anode. AISI 4340, annealed, and AISI 4340, hardened, behaved the same as Fe.

These results appear consistent with a hydrogen embrittlement model of stress corrosion.

**Publications**

"Behavior of Sulfide Electrodes in Aqueous Sodium Chloride Solution," M. Inam Khokhar, E. G. Haney, and Paul Fugassi, Corrosion 26:7, July 1970, pp. 180-182

"Effect of  $\text{H}_2\text{S}$  on Differential Aeration Cells with AISI 4340 Steel Electrodes," M. Inam Khokhar, P. Fugassi, and E. G. Haney, Corrosion 27:3, March 1971, pp. 91-94

## Carnegie-Mellon University

## AN INVESTIGATION OF THE CORROSION AND STRESS-CORROSION BEHAVIOR OF AN Al-Cu ALLOY

R. D. Townsend and J. C. Caron\*

(\* Graduate Student)

## Objective

The purpose of this work was to investigate the corrosion and stress-corrosion behavior of an Al-4/wt-% Cu alloy in a variety of environments.

## Approach

The pitting corrosion of this alloy in a 3.5wt-% NaCl solution when heat treated to produce selected microstructures has been studied as a function of surface condition. The possible degradation of mechanical properties accompanying this pitting has also been determined. The stress-corrosion susceptibility (SCS) of this alloy after being aged for 24 hours at 180° C has been determined as a function of the pH of the NaCl solution. The SCS was also determined for specimens which were tested at pH=1 after receiving the same heat treatment but having the interior of the grains electrically insulated. The SCS of the specimens was determined using a U-bend configuration.

## Achievements

Specimens which were aged at room temperature exhibited non-preferential pitting, and exposure to the NaCl solution for one week resulted in no degradation in mechanical properties. Disruption of the oxide film by scratching caused preferential attack along the scratches. Specimens aged to maximum strength at 180° C showed preferential pitting at the grain boundaries and exposure to the solution resulted in a significant degradation in the mechanical properties. No preferential pitting occurred when the surface of these specimens was scratched. An increase in SCS accompanied a decrease in the pH of the NaCl solution. It was also noted that insulating the grain interiors decreased the rate of cracking. These results would seem to indicate that a hydrogen generation reaction might control SCS in this material.

## Carnegie-Mellon University

**THE DEVELOPMENT OF A MICROSTRUCTURE IN Al-7Zn-2.3 Mg WITH DESIRABLE MECHANICAL PROPERTIES AND RESISTANCE TO STRESS-CORROSION CRACKING**

A. J. DeArdo, Jr., Samuel R. Janis\*, and Richard D. Zordan†

(\* Undergraduate Student)

(† Graduate Student)

**Objective**

A combination of high-yield strength (90% of the T6 condition), a reasonable elongation to failure (5% or more), and adequate stress-corrosion life in a sodium chloride solution (80% to 100% of that typical of overaged specimens) is a desirable combination not currently available. We propose to use our knowledge of the effects of microstructural features on these properties to attempt to achieve this goal.

**Approach**

Previous work has established that the type, size, and spacing of the matrix precipitate controls the degree of stress-corrosion susceptibility of a microstructure through its control of the deformation process. The results of this work suggest that a microstructure hardened by a mixture of large G. P. zones and large  $\eta$  precipitates might well have optimum properties. The large G. P. zones would result in a high-yield strength and the large  $\eta$  precipitates would cause the deformation mode to be rather homogeneous resulting in good ductility and high resistance to stress corrosion.

**Achievements**

A preliminary investigation of the possible heat-treating procedures needed to obtain the mixture of G. P. zones and  $\eta$  precipitates is in progress.

## Carnegie-Mellon University

**THE EFFECT OF MICROSTRUCTURE ON THE MECHANICAL PROPERTIES OF  
Al-7Zn-2.3Mg****A. J. DeArdo, Jr.****Objective**

To investigate both the phenomenological and mechanistic aspects of the effect of microstructure on the mechanical properties of polycrystalline Al-7Zn-2.3Mg.

**Approach**

Previous work in this system has indicated that the strength and ductility of polycrystalline tensile specimens appear to depend on the type, size, and spacing of the matrix precipitate, and not on the width of the precipitate free zone (PFZ). In order to establish more directly how the matrix precipitate controls mechanical properties, certain microstructures having specific properties have been characterized using transmission microscopy. Sheet tensile specimens were heat treated to produce these microstructures, and were then electropolished and deformed. The slip line characteristics at the specimen surface were observed using optical microscopy. Thin foils were taken from these deformed specimens and observed in the electron microscope with the aid of a double tilt stage.

**Achievements**

The experimental work described above is in progress.

**Publications**

"The Effect of Microstructure on the Ductility of Polycrystalline Al-Zn-Mg Alloys," A. J. DeArdo, Jr., and R. D. Townsend, to be submitted for publication

"The Precipitation of an Al-Zn-Mg Alloy Resulting from Double Aging," A. J. DeArdo, Jr., to be submitted for publication



## Carnegie-Mellon University

**THE EFFECT OF MICROSTRUCTURE ON THE FRACTURE TOUGHNESS OF Al-7Zn-2.3 Mg IN AIR AND IN A 3.5% NaCl SOLUTION****A. J. DeArdo, Jr. , and Mohan M. Phadke****Objective**

To investigate the effect of microstructure on the fracture toughness and subcritical crack growth rates in air and in a NaCl environment.

**Approach**

Previous work has shown that when six different microstructures, all having the same yield strength, were tested for stress-corrosion susceptibility (SCS), a wide range of behavior resulted. This previous study was conducted on thin sheet material, and the SCS measured in these experiments was strongly related to the time for the initiation of SC cracks. In order to understand the effect of microstructure on the fracture toughness and subcritical crack growth rate, the six microstructures described above will be tested, using a double cantilever beam type specimen. These fracture toughness experiments will be performed both in air and in an NaCl environment.

**Achievements**

An effort is now in progress to decide on the best specimen configuration to be used. Preliminary work on evaluating the effect of specimen thickness on the response to heat treatment is also in progress.

University of Florida

## INFLUENCE OF CHROMIUM CONTENT ON DOMAINS OF PASSIVITY FOR BINARY IRON-CHROMIUM ALLOYS

Ellis D. Verink, Jr., Marcel Pourbaix\*, R. L. Cusumano†, and K. D. Eifird‡

(\* Consultant, CEBELCOR, Brussels, Belgium)

(† Graduate Student)

### Objective

Explain the tendency for pitting and crevice corrosion of iron-chromium alloys in terms thermodynamic arguments supported by experimental verification. Seek experimental evidence which may interconnect susceptibility to localized forms of attack such as pitting and crevice corrosion with other forms of corrosion such as stress corrosion.

### Approach

Construct a three-dimensional Pourbaix Diagram (potential-pH-composition) delineating domains of immunity, corrosion, and passivity as a function of variation in chromium content for binary Fe-Cr alloys. Determine the variation of the protection potential with chromium content.

Six binary Fe-Cr alloys ranging in chromium content from 0.5-25 weight percent were investigated using potentiokinetic measurements employing the electrochemical hysteresis method in saline solutions ranging in pH from 4.5 to 11, and in chloride concentrations from nil to saturated at room temperature. The results were plotted on potential versus pH coordinates to form experimentally-determined Pourbaix Diagrams for each alloy. Corresponding features were cross connected between diagrams to form the three-dimensional diagram. Particular attention was given to determining the protection potential under each experimental condition.

### Achievements

The influence of increasing content of chromium in binary iron-chromium alloys is: (1) to reduce the potential-pH domain of active corrosion, (2) to broaden the pH domain of passivity, (3) to widen the potential range of freedom from pitting, (4) to reduce the corrosion rate, (5) gravimetric measurements confirm the "Immunity Potential" approximates the intersection of the Zero Current Potential locus and the equilibrium hydrogen evolution line, and (6) physical model of three-dimensional Pourbaix Diagram completed. The protection potential for these alloys is not strongly dependent on chromium content.

### Publications and Theses

Excerpts of certain portions of the work have been included in the following publications: M. Pourbaix, Rapport Technique CEBELCOR RT 157 (1969); Resumes des Communications, Symposium Belgo-American, Brussels, Sept. 3-4, 1969; CEBELCOR Rapports Technique RT 165 (1969); "The Establishment of a Three-Dimensional (Potential-pH-Composition) Diagram for Binary Fe-Cr Alloys in 0.1 Molar Chloride Solutions," R. L. Cusumano, M.S. Thesis, March 1971; "Use of Electrochemical Hysteresis Techniques in Developing Alloys for Saline Exposures," E. D. Verink and M. Pourbaix, submitted to NACE for publication in Corrosion.

**Invited Talks**

- M. Pourbaix, 18th General Assembly of CEBELCOR, May 25, 1970, Brussels, Belgium
- M. Pourbaix, NACE Research Conference, Cleveland, Ohio, March 1969
- M. Pourbaix, NACE Research Conference, Philadelphia, Pa., March 1969
- E. D. Verink, Jr., OSW Research Conference, Freeport, Texas, April 10, 1970
- E. D. Verink, Jr., (presented by Pourbaix) and M. Pourbaix, 1970 CEBELCOR Corrosion Week, Brussels, Sept. 1970
- E. D. Verink, Jr., and M. Pourbaix, Annual Meeting NACE, Chicago, Illinois, March 1971

University of Florida

## INFLUENCE OF IRON ADDITIONS ON THE ELECTROCHEMICAL BEHAVIOR OF 90-10 Cu-Ni ALLOYS

Ellis D. Verink, Jr., G. M. Schmid, M. Pourbaix\*, and P. A. Parrish†

(\*Consultant, CEBELCOR, Brussels, Belgium)

(†Graduate Student)

### Objective

Develop methods for construction of three-dimensional Pourbaix Diagrams from experimental observations. Delineate domains of freedom from pitting and denickelification for 90-10 Cu-Ni alloy composition containing various levels of added iron.

### Approach

Potentiokinetic techniques employing electrochemical hysteresis methods were used to establish rupture potentials, protection potentials, and passivation potentials in saline solutions for two alloys of the 90-10 Cu-Ni type, one without added iron, the other containing 1.46 wt-%. Solution variables included chloride contents from nil to saturated at room temperature in aqueous solutions ranging in pH from 4.5 to 11 inclusive. These data were correlated in experimental Pourbaix Diagrams.

### Achievements

The experimental methods and data manipulation necessary for the construction of experimental Pourbaix Diagrams were evolved. The protection potential was shown to be independent of pH and iron content (within this range of composition). It was possible to predict conditions leading to denickelification from analysis of Pourbaix Diagrams. X-ray analysis plus scanning electron microscopy provided evidence regarding the mechanisms of corrosion.

### Publications and Theses

"Use of Pourbaix Diagrams in Predicting Susceptibility to Dealloying Phenomena," E. D. Verink and P. A. Parrish, *Corrosion* 26, 5, 1970

"Use of Experimentally Determined Pourbaix Diagrams to Elucidate the Role of Iron in the Passive Behavior of Copper-Rich Alloys Containing Nickel," P. A. Parrish, M. S. Thesis, June 1970

"Use of Electrochemical Hysteresis Techniques in Developing Alloys for Saline Exposures," E. D. Verink and M. Pourbaix, submitted to NACE for publication in *Corrosion*

### Invited Talks

M. Pourbaix, 18th General Assembly of CEBELCOR, May 25, 1970, Brussels, Belgium

E. D. Verink, OSW Research Conference, Freeport, Texas, April 10, 1970

E. D. Verink, Florida General Conference, NACE, Key Biscayne, Florida, November 1969

M. Pourbaix, 1970 CEBELCOR Corrosion Week, Brussels, Belgium, September 1970

E. D. Verink and M. Pourbaix, Annual Meeting NACE, Chicago, Illinois, March 1971

University of Florida

## INCLUSION OF KINETIC INFORMATION IN EXPERIMENTALLY DETERMINED POURBAIX DIAGRAMS

Ellis D. Verink, Jr., Marcel Pourbaix\*, K. K. Starr†, P. A. Parrish†, K. D. Eiford†, R. L. Cusumano†, and J. A. Snodgrass†

(\* Consultant, CEBELCOR, Brussels, Belgium)

(† Graduate Student)

### Objective

Develop a technique for including kinetic information in experimentally determined Pourbaix Diagrams for engineering alloys.

### Approach

Potentiokinetic polarization curves (potential vs. current density) were available for six Fe-Cr alloys and two Cu-Ni alloys from electrochemical hysteresis studies in saline solutions of a range of pHs. The corrosion rate at a given potential is proportional to the current density. It is possible to tabulate the potential at which a selected value of current density (e.g.,  $10^{-2}$  amps/cm<sup>2</sup>) occurs for a given alloy at a given pH. Repetition of this procedure through the range of pHs provides data which when plotted on the experimental Pourbaix Diagrams (usually as the logarithm) gives a locus of points having the same corrosion rate. Selection of several current densities provides data for construction of a family of iso-corrosion "trajectories." This method was originally suggested by Pourbaix.

### Achievements

The observed values of current density obtained from potentiokinetically produced polarization curves is sensitive to the scan rate. Therefore, scan rates must be equal if data from different experiments are to be compared. The corrosion rates obtained in such tests must be "calibrated" by long term tests if quantitative data are desired. However, the data may be used directly for comparison of the relative corrosion behavior of chromium additions to Fe-Cr binary alloys. Another important use of such data has resulted from this research. In alloy systems where the boundary between a region of active corrosion and a region of passivity is bounded by a vertical line on the Pourbaix Diagram (e.g., independent of potential), the iso-corrosion trajectories may be used to establish the critical pH at which this transition in behavior occurs. The 90-10 Cu-Ni experimental Pourbaix Diagram is an example.

### Publication and Thesis

"Use of Experimentally Determined Pourbaix Diagrams to Elucidate the Role in the Passive behavior of Copper-Rich Alloys Containing Nickel," P. A. Parrish, M. S. Thesis, June 1970

**"Use of Electrochemical Hysteresis Techniques in Developing Alloys for Saline Exposures," E. D. Verink and M. Pourbaix, submitted to NACE for publication in Corrosion**

#### **Invited Talks**

**E. D. Verink, OSW Research Conference, Freeport, Texas, April 10, 1970**

**M. Pourbaix, 18th General Assembly of CEBELCOR, Brussels, Belgium, May 25, 1970**

**M. Pourbaix and E. D. Verink (presented by Pourbaix), 1970 CEBELCOR Corrosion Week, Brussels, Belgium, September 1970**

**E. D. Verink and M. Pourbaix, Annual Meeting NACE, Chicago, Illinois, March 1971**

University of Florida

## ELECTROCHEMICAL HYSTERESIS METHOD FOR DELINEATING DOMAINS OF PITTING IMMUNITY ON POURBAIX DIAGRAMS

Ellis D. Verink, Jr., G. M. Schmid, M. Pourbaix\*, and K. K. Starr†

(\* Consultant, CEBELCOR, Brussels, Belgium)

(† Graduate Student)

### Objective

The protection potential has been observed to have a direct relationship to the potential inside active pits, crevices, and stress-corrosion cracks. The purpose of this research is to establish the role of chloride adsorption-desorption phenomena in the mechanisms involved.

### Approach

Through use of potentiodynamic methods, establish rupture potential and protection potentials for iron-12chromium alloy as a function of pH in saline solutions. Hold the potential at a selected value so as to initiate a pit and allow the pit to perforate the specimen. Embedded Ag-AgCl (or Pd-H<sub>2</sub>) electrodes are used to determine the chloride content (or the pH) in the active pit at time of perforation. Experiments over the range of electrochemical hysteresis will provide evidence as to whether the observed hysteresis is related to a chloride adsorption-desorption phenomenon as proposed by G. L. Schmid, and/or a pH effect or both. Physical confirmation of morphological aspects is being sought by scanning electron microscopy.

### Achievements

Values of  $E_R$  and  $E_P$  have been established for a range of pHs in saline solutions. The design of the embedded Ag-AgCl electrode has been tested and indicates that chloride enrichment occurs in an active pit in saline solutions. This result is consistent with prognostications in the literature. Several modifications in instrumentation and technique are in progress to refine the measurements. After a number of experimental changes, this aspect of the work was judged to be unfruitful and has been abandoned in favor of work on artificial crevices.

### Publications and Theses

None

### Invited Talks

E. D. Verink, Jr., Florida General Conference NACE, Key Biscayne, Florida, November 1969



## University of Florida

**INFLUENCE OF CREVICES ON THE CORROSION BEHAVIOR  
OF ALLOYS**

Ellis D. Verink, Jr., K. D. Efird†, K. K. Starr†, and M. Pourbaix\*

(\* Consultant, CEBELCOR, Brussels, Belgium)

(† Graduate Student)

**Objective**

Devise a relatively simple laboratory test method which faithfully reproduces conditions found in crevices.

**Approach**

Improve on methods of crevice corrosion testing described in the literature by providing capability for separate monitoring of "crevice" and "bulk" with respect to pH, chloride content, metal ion content in solution, current flow, potential, all as a function of time. Permit use of sufficiently large specimens to permit detailed examinations and analysis.

**Achievements**

A new electrochemical test cell has been developed which permits monitoring of all desired variables, and employs specimens capable of detailed examination by x-ray, SEM, metallographic and optical techniques. Drastic variations in pH and composition of electrolytes in crevices as compared to the bulk were confirmed. The beneficial influence of pretreatment under specific conditions of potential and pH as a means of extending usefulness of materials is suggested.

**Thesis**

"Crevice Corrosion of a Copper-Nickel Alloy and Its Relationship to the Experimental Pourbaix Diagram," K. D. Efird, M. S. Thesis, December 1970

**Invited Talk**

E. D. Verink, Jr., Annual Meeting NACE, Chicago, Illinois, March 1971

## Georgia Institute of Technology

## SURFACE CHEMISTRY AND PHYSICS IN STRESS-CORROSION CRACKING

Edwin J. Scheibner and Gary W. Simmons

## Objectives

Our goal has been to determine the fundamental properties of metals and alloys that are of technical importance to the ARPA stress-corrosion studies. Titanium, aluminum, and iron-based alloys have been of particular interest in this program. We have directed our efforts primarily to studies of pure titanium.

## Approach

The principal technique applied in our studies has been the scattering of low energy electrons from metal surfaces. Structure of alloy surfaces, order-disorder transitions at surfaces, and changes in structures due to chemisorption and to corrosion are determined by the elastically diffracted electrons. Detection and energy analysis of Auger electrons provides an analytical method of monitoring the surface composition. Measurement of the inelastic (characteristic energy loss) spectrum yields information about the fundamental electron properties of the bulk metal and its surface. Experiments are conducted in an ultra-high vacuum ( $10^{-10}$  torr) system, and the samples are exposed to spectroscopically pure gases. Surface samples are prepared by heating and argon ion bombardment of bulk single crystals as well as by epitaxial growth of metals that are evaporated in situ.

## Achievements

The difficulties encountered in the preparation of clean surfaces of titanium due to the high reactivity of this metal and to the stability of interstitial impurities are of significant interest. Auger spectroscopy showed that the titanium surfaces were not clean after extensive ion bombardment and heating. The principal impurities found after this treatment were sulfur, carbon, and oxygen. This problem encountered with bulk samples led to the development of techniques for growing epitaxial single crystals of titanium in situ. We found that clean single crystal titanium surfaces with a (0001) orientation could be grown on (111) MgO surfaces. Clean surfaces were obtained only for depositions that were made with pressure increases held to the  $10^{-9}$  torr range.

An order-disorder transition was observed for oxygen in titanium. For temperatures below  $530^{\circ}\text{C}$  the oxygen in solution was found to occupy alternate layers of octahedral interstices along the c-axis. Above this temperature the oxygen entered every layer of octahedral interstices.

The inelastic spectrum for clean evaporated titanium films was investigated as a function of oxygen adsorption. The energy for the bulk plasma excitation was determined, and an energy loss peak associated with a surface plasmon was identified. The intensity of the surface loss was found to be sensitive to oxygen coverages as low as 4 per cent.

**Publications and Presentations**

"Auger Electron Spectroscopy and Inelastic Electron Scattering in the Studies of Metal Surfaces," G. W. Simmons and E. J. Scheibner, accepted by Journal of Colloid and Interface Science

"Order-Disorder Phenomena in the Surface of  $\alpha$ -Titanium Oxygen Solid Solutions," G. W. Simmons and E. J. Scheibner, accepted by ASTM Journal of Materials

"Preparation and Characterization of Titanium (0001) Surfaces," G. W. Simmons, submitted to Vacuum Science and Technology

"Characteristic Energy Loss Spectra of Titanium, Vanadium and Chromium." G. W. Simmons, submitted to Journal of Applied Physics

"Techniques of Surface Physics Applied to Stress Corrosion," G. W. Simmons, H. E. Grenga, and R. F. Hochman, presented to ASM, Los Angeles, March 1970; being revised for publication

"Characterization and Reactivity of Titanium Surfaces," G. W. Simmons, Lehigh University, Bethlehem, Pennsylvania, and E. J. Schiebner, Georgia Institute of Technology, Atlanta, Georgia. Conference on Stress Corrosion Cracking Mechanisms in Ti Alloys, to be published by the NACE

## Georgia Institute of Technology

## A STUDY OF THE ELECTROCHEMICAL BEHAVIOR OF TITANIUM-ALUMINUM BINARY AND COMMERCIAL ALLOYS UNDER STRESS

R. F. Hochman, A. Pourbaix†, M. Marek†, R. Piccinini\*†, F. C. Lin\*, and K. C. Chen

(\* Graduate Student)

(† On support outside ARPA project)

## Objective

The purpose of this program is to devote a strong effort in studying the electrochemical behavior of Ti-Al alloys in corroding solutions when subjected to stresses above and below the yield point.

## Approach

Both dynamic and static tensile and bending tests are used with areas of a given size masked on the surface for electrochemical polarization studies. These areas are normally in the point of maximum stress either by design of the testing procedure or by design of the specimen.

Another approach was the design and use of a special cell to simulate conditions of an isolated cell, i.e., pit or crack tip. Wax coated electrodes of Ti and Ti-Al alloys were placed in a small cell of 3.5% NaCl solution and connected through a porous glass plug to a much larger electrode in the same solution. The circuit was completed with an external metal connection. Once the circuit was closed a motorized diamond scratching device was used to continuously scratch the wax coated specimen which rapidly became anodic. The pH in the isolated solution, the ions in solution and the potential difference in the cell were all determined.

## Achievements

In evaluating the polarization curves for Ti-Al alloy specimens, it was found that the anodic polarization curves in 3.5% NaCl have a very small active region. However, large increases in the active region occurred during plastic deformation. It is interesting to note that this did not occur in a  $K_2SO_4$  solution with specimens in plastic strain. It appears that in NaCl solutions, film rupture and dislocation pile-ups in a local region near the free surface enhances the reactivity. One reaction appears to be  $2Ti + 4Cl^- \rightarrow 2TiCl_4 + 4e^-$ ; this has been deduced from potentials in the active region.

In the simulated isolated cell, the results on pure titanium and some titanium-aluminum alloys, in a 3.5% sodium chloride solution at room temperature (initial pH 6.5) show a sharp increase in acidity of the solution at the scratched electrode. The lowest pH recorded thus far was 1.87. Comparative tests were conducted on a series of titanium alloys, both susceptible and non-susceptible to SCC in salt water. Once the pH dropped below 2.0 Ti ions could be found in the solution. The potential difference between the two electrodes during the experiment reached 0.65 volts.

An International Symposium on Stress Corrosion Mechanism in Titanium Alloys was held at Georgia Tech, January 26, 28 and 29, 1971, cochaired by R. F. Hochman and J. C. Scully. The proceedings will be published by the NACE.

#### Publications and Theses

Thesis, F. C. Lin, "An Investigation of the Electrochemical Factors Involved in the Stress Corrosion Cracking of Titanium Alloys in Salt Solutions." June, 1970

Thesis, R. Piccinini, "Electrochemistry of Stress Corrosion Cracking of Titanium Alloys in Chloride Environments." In preparation

"Electrochemical Behavior of Ti-Al at Low pH and Low Electrode Potentials," A. J. E. Pourbaix, M. Marek, R. F. Hochman, Georgia Institute of Technology, Atlanta, Georgia, Proceedings, Conference on Stress Corrosion Cracking Mechanism in Ti Alloys, to be published by the NACE

"Stress Corrosion Mechanism in Titanium Alloys," edited by R. F. Hochman and J. C. Scully. A Symposium to be published by the NACE

## Georgia Institute of Technology

**FIELD EMISSION STUDIES OF THE SURFACE CHARACTERISTICS OF SUSCEPTIBLE AND NON-SUSCEPTIBLE ALLOYS**

H. E. Grenga, R. F. Hochman, and S. Chakraborty\*

(\* Graduate Student)

**Objective**

To study the surface reactions of Ti, Ti-Al alloys and steel.

**Approach**

With the FEM one can measure the relative work functions of different crystallographic regions of a metal, both in the clean condition and with adsorbed gases. The adsorption and diffusion phenomena can also be studied by direct observation to contract changes in the image. The activation energies for diffusion over different crystallographic regions can be determined and used to ascertain relative binding energies of the adsorbed species. A necessary condition for obtaining quantitative information from these techniques is that a clean surface be prepared. The difficulties encountered in preparing clean titanium were discussed under FIM research.

A second approach which is presently underway is to use the hydrogen contaminated specimens prepared by electrolytic etching in a solution of hydrofluoric and nitric acids in the following experiments:

- a) Measure relative work functions of the specimen as prepared above.
- b) Heat the specimen and measure the amount of hydrogen evolved with PPG tube.
- c) Measure the relative work functions again.
- d) Repeat b) and c).

From the above measurements the effect of hydrogen on the work function can be determined and used to obtain information on the effect of hydrogen on the bonding in titanium.

**Achievements**

A special FEM laboratory was set up and a microscope designed and built for this work. Initial data on hydrogen and oxygen effects have been obtained.

Due to the progress in FIM experiments on surface films on the interaction of hydrogen with titanium, and on obtaining high resolution images of titanium, efforts have been concentrated primarily on field-ion microscopy. The field emission techniques have been developed meanwhile using a more refractory type material. These results have shown that adsorption states can be correlated with crystallographic regions on the metal surface by using field desorption techniques to remove adsorbed gases.

**Publications and Presentations**

**"A Review of Field-Ion and Field-Emission Microscopy Studies of Corrosion," R. F. Hochman and H. E. Grenga, paper presented to the ASTM Fall Meeting, Atlanta, 1968**

**"Gas-Metal Interactions: Field-Ion and Emission Microscopy," H. E. Grenga and R. F. Hochman, paper presented to FIM Conference at Georgia Tech, May 1968; Conference Proceedings, Georgia Tech, December, 1969**

**Field-Ion Microscopy in Physical Metallurgy and Corrosion, Conference Proceedings, R. F. Hochman, E. W. Muller and B. Ralph, Georgia Tech., December 1969**

**"The Application of Field-Ion and Field-Emission Microscopy to Surface Studies," H. E. Grenga and R. F. Hochman, paper to be presented at the 44th Colloid Symposium, Bethlehem, Penn., June, 1970; Proceedings to be published**

**"Techniques of Surface Physics Applied to Stress Corrosion," G. W. Simmons, H. E. Grenga, and R. F. Hochman, paper presented at Westec Meeting ASM, Los Angeles, March 1970; Proceedings to be published**

**H. E. Grenga, R. F. Hochman, and R. Kumar, "Surface Properties of Titanium and Titanium Alloys," paper presented to the International Symposium on Stress Corrosion Mechanisms, Atlanta, 1971, NACE, in press**

**S. Chakraborty, "Field Emission Studies on the Adsorption of CO on Ruthenium," Thesis, Georgia Tech, Atlanta, 1971**

## Georgia Institute of Technology

FIELD ION MICROSCOPY OF TITANIUM,  $\text{Ti}_3\text{Al}$ , AND STEELS

H. I. Grenga, R. F. Hochman, and R. Kumar\*

(\* Graduate Student supported outside ARPA Project)

## Objective

The objective of this research is to study the effect of gases particularly hydrogen and oxygen, on the bonding in titanium,  $\text{Ti}_3\text{Al}$ , and high strength steels.

## Approach

Extremely fine (100°A) specimen tips were prepared by electrolytic etching techniques. Helium field-ion microscopy at liquid hydrogen and helium temperatures was used to obtain images with atomic resolution of the specimen surface. Impurities could be discerned in these images. The effect of impurities on the bonding was determined qualitatively from FIM observations by comparing the evaporation fields of regions with different impurity concentrations. A more quantitative approach would require that an image of clean metal or alloy be obtained first, then exposed to gas and finally the change in evaporation field measured.

Hydrogen-ion microscopy at liquid nitrogen temperature has also been used in these studies. While this technique does not yield atomic resolution, information on surface films and on the effect of hydrogen on the surface energy of titanium was obtained.

## Achievements

Surface films were formed on electropolished titanium specimens. These surface films appeared to be different from those formed by oxidation in air at elevated temperatures in the following ways: the surface films resulting from electropolishing showed a much higher degree of epitaxy and probably were not the normal  $\text{TiO}_2$ .

It has been found that extensive contamination by hydrogen and oxygen occurs even under conditions previously considered to give negligible contamination.

Heating specimens produced heavier oxygen contamination in the bulk, while field etching in hydrogen removed this oxide layer and gave reasonably good images with helium-ion microscopy. Using a qualitative approach, it was found that oxygen and hydrogen decrease the bond strength in titanium and ordered  $\text{Ti}_3\text{Al}$ . The degree of oxygen contamination and the effect of oxygen on the bond strength was less for ordered  $\text{Ti}_3\text{Al}$  than for titanium.

The most recent results show that high quality images of titanium can be obtained with helium ion microscopy at liquid helium temperatures using the microchannel plate converter. Comparison of helium and hydrogen ion microscopy results have shown that hydrogen preferentially lowers the metallic binding or surface energy on  $\{10\bar{1}1\}$  and  $\{0001\}$  planes. Platelets were observed in hydrogen-ion images only and were found to be lying parallel to a plane in the zone passing through the  $(0001)$ - $(11\bar{2}0)$  planes. These platelets may represent thin hydrides or hydrogen segregation at defect sites, formed by the interaction of titanium with hydrogen during field-ion microscopy.



**Publications and Presentations**

**"Field-Ion Images from Ordered  $\text{Ni}_4\text{Mo}$ ," B. G. LeFevre, H. E. Grenga, and B. Ralph, Phil. Mag. 18, 1968, pp. 1127-1141**

**"A Review of Field-Ion and Field Emission Microscopy Studies of Corrosion," R. F. Hochman and H. E. Grenga, paper presented to the ASTM Fall Meeting, Atlanta, 1968**

**Field-Ion Microscopy in Physical Metallurgy and Corrosion, Conference Proceedings, Robert F. Hochman, E. W. Muller and B. Ralph, Georgia Tech, December, 1969**

**"Gas-Metal Interactions: Field-Ion and Emission Microscopy," H. E. Grenga and R. F. Hochman, FIM Conference at Georgia Tech, May, 1968; Conference Proceedings published**

**"Field-Ion Microscopy of Titanium and Ordered  $\text{Ti}_3\text{Al}$ ," H. E. Grenga, paper presented to 16th Field Emission Symposium, Pittsburgh, Sept. 1969**

**"The Application of Field-Ion and Field-Emission Microscopy to Surface Studies," H. E. Grenga and R. F. Hochman, paper to be presented at the 44th Colloid Symposium, Bethlehem, Penn., June, 1970; Proceedings to be published**

**"Techniques of Surface Physics Applied to Stress Corrosion," G. W. Simmons, H. E. Grenga, R. F. Hochman, paper presented at Westec Meeting ASM, Los Angeles, March, 1970; Proceedings to be published**

**H. E. Grenga, R. F. Hochman and R. Kumar, "Properties of Titanium and Titanium Alloy Surfaces," paper presented to the International Symposium on Stress Corrosion Mechanisms in Titanium Alloys, Atlanta, 1971, NACE, in press**

**R. Kumar, "Field-Ion Microscopy Studies on Surface Properties of Titanium," Thesis, Georgia Tech, Atlanta, 1971**

**B. N. Ranganathan and H. E. Grenga, "Field-Ion Microscopy of Steels," paper presented at the Westec Conference, Los Angeles, 1971**

**B. N. Ranganathan and H. E. Grenga, "Field-Ion Microscope Studies of Tempered Martensite," paper presented at TMS Spring Meeting, Atlanta, 1971**

Georgia Institute of Technology

## **SLOW STRAIN RATE HYDROGEN EMBRITTLEMENT AND STRESS-CORROSION CRACKING IN Ti-Al BINARY ALLOYS**

**E. A. Starke, Jr., R. F. Hochman, and D. A. Mauney\***

(\*Graduate Student)

### **Objective**

This study was undertaken in an effort to define the possible role of hydrogen in the stress-corrosion cracking (SCC) of Ti-Al binary alloys.

### **Approach**

The role of hydrogen was studied by comparing fracture characteristics of SCC to slow strain rate hydrogen embrittlement (SSRHE) in three Ti-Al binary alloys (2.5, 5.0, and 8.0 wt-% Al) using electron fractography, electron microscopy, and x-ray techniques.

### **Achievements**

The similarities between SCC and SSRHE failures in Ti-5 and 8 wt-% Al alloys strongly suggest that hydrogen plays a significant role in the SCC process. The present observations indicate that the precipitation of hydrides on coplanar dislocations is related to the mode of SCC and SSRHE failure in Ti-Al alloys. The cleavage habit plane observed for SCC, which is close to but not the basal plane, appears to be the prominent fracture plane for all brittle failures of these Ti-Al binary alloys.

### **Publications**

"Explanation of the Cleavage Plane in Stress Corrosion Cracking of Alpha Phase Titanium-Aluminum Alloys," David A. Mauney and E. A. Starke, Jr., *Corrosion* **25**, 1969, p. 177

"Slow-Strain-Rate-Hydrogen Embrittlement and Stress Corrosion Cracking in Ti-Al Binary Alloys," David A. Mauney, M. S. Thesis, June 1969

"Hydrogen Embrittlement and Stress Corrosion Cracking of Ti-Al Binary Alloys," D. A. Mauney, Alcoa Research Laboratories, New Kensington, Pennsylvania, E. A. Starke, and R. F. Hochman, Georgia Institute of Technology, Atlanta, Georgia. Symposium on Stress Corrosion Cracking Mechanisms in Ti Alloys. To be published by the NACE.

## Georgia Institute of Technology

## THE STRESS-CORROSION SUSCEPTIBILITY OF HIGH STRENGTH STEELS

R. F. Hochman, P. Kalafonos\*, J. Rinker\*, and M. Marek†

(\*Graduate Student)

(†Graduate Student, Part-Time)

## Objective

To determine the stress-corrosion cracking characteristics of high strength maraging stainless steel (Almar 362) and the galvanic effects of Cd on high yield strength 4340.

## Approach

Tests in these studies include anodic-polarization studies on the maraging stainless steel under stress using side-notched 1 in. wide specimens of Almar 362. Time to failure was studied as a function of applied stress and for various heat treatments and applied external currents.

To evaluate the role of cadmium plating on 4340 cantilever beam type notched specimens were prepared of 250,000 psi yield strength material. Samples were prepared as heat treated, cadmium plated, cadmium plated and baked, and cadmium plated, baked and then the bottom of the notch scribed to remove the cadmium, followed by exposure to 3-1/2% sodium chloride solution.

## Achievements

Significant increases in tensile strength were accomplished by cold working the Almar 362 before aging. The resulting tensile strength levels were as high as 240,000 psi. Yield strength values as high as 230,000 psi were obtained by this same treatment. In addition, failure as a function of applied stress was determined for numerous heat treatments and various applied currents. Material aged at higher temperatures (1150°C) was always found to be less susceptible than the material aged at lower temperatures (900°C). Potential-time curves showed that cracking occurred under both anodic and cathodic potentials in chloride solutions containing acetic acid or  $\text{SeO}_2$ . Without these activation agents, at room temperature failure did not occur. Impressed anodic currents of a few small MA increased the life of the material, whereas impressed cathodic current decreased the time to failure. The latter is strong evidence to support the conclusion that in such media Almar 362 failed by hydrogen embrittlement cracking. Scanning electron microscopy studies of the fractures showed little difference between anodic and cathodic cracking which is in agreement with the conclusions of hydrogen embrittlement.

For the 4340 specimens, cadmium plated with no baking versus cadmium plated, baked, cadmium plate removed at the bottom of the notch and exposed to 3.5% NaCl, broke in very short periods of time compared to standards. Fractographic examination revealed typical intergranular fractures for both types of tests typical of hydrogen embrittlement and stress-corrosion cracking fractures.

In preliminary electrochemical studies, the open circuit potential between cadmium plated material and 4340 in the 250 psi yield range was measured and found to be 270 millivolts with the steel being cathodic to the cadmium plating. This figure is reduced by polarization to approximately 150 millivolts after an hour and a half and then remained essentially constant. Further studies to develop the actual electrode reactions are now under way to determine if hydrogen is evolved on the 4340 which would indicate hydrogen adsorption in the crack tip of the notched specimens.

A unique discovery was made using low embrittlement cadmium plating. Unbaked notched bend samples readily broke at 50% of the yield strength after plating. After baking these samples exhibited infinite life at the same load level. However, without scratching the sample life dropped to the prebaked value when immersed in a 3.5% NaCl solution. It appears the porosity of the plating, which makes it easier to bake-out, actually enhances the stress-corrosion cracking and hydrogen re-embrittlement. A very serious consideration for high strength steels for aircraft.

#### Publications and Thesis

"Stress Corrosion Cracking in Almar 362 Mar-Ageing Stainless Steel," P. Kalafonos, Thesis, Sept. 1969.

"Stress Corrosion Cracking of Almar 362 Mar-Ageing Stainless Steel," P. Kalafonos and R. F. Hochman, to be submitted for publication

"Stress Corrosion Cracking Susceptibility of Cadmium Plated High Strength 4340," J. Rinker and R. F. Hochman, revised and submitted for publication as a Note in Corrosion

## Georgia Institute of Technology

**APPLICATION OF ULTRASONIC AND ACOUSTIC EMISSION TESTING METHODS TO STRESS-CORROSION CRACKING****M. E. Sikorski and L. H. Glassman****Objective**

To study the applicability of ultrasonic flaw detection methods and acoustic emission to stress-corrosion cracking (SCC) measurements. In particular to devise methods of measuring fast growth rates and detecting cracking thresholds.

**Approach**

The conventional cantilever beam SCC test was instrumented with an ultrasonic flaw detecting transducer and an accelerometer for acoustic pickup. Thus the performance of these devices could be correlated with data obtained from many sources.

**Achievements**

The application of ultrasonic flaw detection techniques has led to the development of the ultrasonic contourograph, a unique method for displaying the progress of a rapidly growing crack.

An acoustic emission facility has been established and threshold detection of SCC agrees with the same data derived from conventional tests. In addition, acoustic emission may be used to record the progress of SCC with greater resolution than conventional techniques, although accurate rate calibrations are difficult to achieve.

Georgia Institute of Technology

## MICROMECHANICAL STUDIES OF METALS AND STRESS-CORROSION CRACKING SUSCEPTIBLE AND NON-SUSCEPTIBLE ALLOYS

E. A. Starke, Jr., and B. R. Livesay\*

(\* Graduate Student)

### Objective

To develop micromechanical techniques for the measurement and analysis of the effect of surface conditions on the mechanical behavior of metals and alloys.

### Approach

To obtain an understanding of the fundamental mechanisms responsible for stress-corrosion cracking (SCC), experiments have been designed to make mechanical property-environment correlations on materials sufficiently thin so that the initial stages of the process are not completely masked by the bulk properties of the remaining unaffected material. Samples of thin metals and alloys, with and without special coatings, are stressed in either air or liquid environments. Correlations are then made between the measured mechanical parameters, such as yield stress, and the imposed environmental conditions. The major thrust of this effort has ultimately been directed towards measurements on carefully thinned copper single crystal samples with certain well-defined coatings.

### Achievements

During the course of this effort a micromechanics facility has been established for making environmental mechanical property measurements on very thin samples in tension, bending, and torsion modes. Several unique sample preparation techniques have been developed for obtaining thinned alloys and pure copper single crystals and for unsupported metal oxide films. Although the instrumentation developed in this laboratory makes possible a number of potentially very useful experiments, the limited funding narrowed indepth studies to the copper thin single crystal surface investigations which is the subject of Mr. Livesay's Ph.D. Thesis. Initial results indicate that the shear modulus of a surface film has a large effect on both the yield strength and work hardening characteristics of the substrate.

### Publications and Presentations

"Micromechanical Studies of High Strength Titanium Alloys," B. R. Livesay, 1968 ARPA Annual Review May 14, 1968, Georgia Tech, Atlanta, Georgia

"Dislocation Interactions at Surfaces," B. R. Livesay, Thesis, Georgia Institute of Technology, Atlanta, Ga., July, 1971

Several papers will be submitted upon the completion of Mr. Livesay's thesis; one will be concerned with the results of the experiments and another with one of the micromechanics instruments

## Lehigh University

**THE RELATIONSHIP BETWEEN STRESS-CORROSION CRACKING KINETICS IN ALUMINUM ALLOY 7075-T6 AND THE CRACK TIP STRESS INTENSITY**

John D. Wood and A. P. Popichak\*

(\* Graduate Student)

**Objective**

Fracture mechanics concepts were used to determine the effect of crack tip stress intensity on the stress-corrosion cracking (SCC) in 7075-T6 aluminum alloy.

**Approach**

The behavior of 7075-T6 aluminum alloy was examined under the influence of stress and immersion in aqueous 3.5% NaCl solution. The specimen was oriented to stress in the short-transverse direction and was of a configuration such that it could be treated from the discipline of fracture mechanics as a single-edge notched specimen. Crack growth as a function of time was determined from optical measurements and subsequently converted to crack-growth rate as a function of time.

**Achievements**

The main conclusions of this research were: 1) In the system tested, crack-growth rates bore no simple relation to the parameters of fracture mechanics; the growth rates were independent of the crack tip stress intensity. 2) Agitation of the solution caused more rapid crack growth by approximately an order of magnitude. 3) Removing part of the load from a growing crack caused the growth to cease even though the remaining load was such that it was sufficient to cause crack growth in another similar specimen.

**Theses**

"A Study of the Stress Corrosion Cracking of 7075-T6 Aluminum Alloy Using Fracture Mechanics Concepts," Andrew Popichak, M. S. Thesis, June 1969

**Presentations**

Thesis presented by A. P. Popichak at the Winter Meeting of AIME, New York, February 1968

"Kinetics of Stress Corrosion Cracking in High Strength Aluminum Alloy," presented by J. D. Wood at Fall Meeting of ASTM, Atlanta, Oct. 1968

"Kinetics of Stress Corrosion Cracking," presented by J. D. Wood at

- a) Naval Air Development Center, Philadelphia, Pa., April 1969
- b) Jackson Laboratories, E. I. duPont, Deepwater, N. J. May, 1969
- c) Reynolds Metals Research Laboratory, Richmond, Va., Jan., 1970
- d) Cartech Corporation, Reading, Pa., Jan. 1970

Lehigh University

**THE EFFECT OF ELECTROCHEMICAL VARIABLES ON THE STRESS-CORROSION CRACK GROWTH RATE OF 4340 STEEL IN SALT WATER**

J. D. Wood and A. A. Sheinker\*

(\* Graduate Student)

**Objective**

The purpose of this study is to determine the influence of environmental factors such as solution pH, electrode potential, and dissolved oxygen content, on the relationship between the stress-corrosion crack-growth velocity and the stress intensity factor (K) for 4340 steel in an aqueous solution of sodium chloride.

**Approach**

The relationship between stress-corrosion crack-growth rate and stress intensity factor (K) is determined by subjecting fatigue-precracked cantilever bend specimens to a constant load while immersed in the corrosive solution, and monitoring crack propagation with a NASA-type displacement gage mounted on the specimen. Since K increases with increasing crack length for a cantilever bend specimen under constant load, the crack growth rate is obtained over a wide range of K in each test. The pH, electrode potential, and dissolved oxygen content of the solution are maintained constant during each test. Thus, the relationship between crack growth rate and stress intensity factor is determined for a given set of external electrochemical conditions in each test. It is recognized, based on the work of B. F. Brown, that external variables may have a minor influence on the solution chemistry within the growing crack.

**Achievements**

Precracked specimens of AISI 4340 steel, heat treated to a yield strength of about 250 ksi, were used in order to utilize the stress intensity factor K to characterize the mechanical driving force for crack propagation. The crack growth rate rather than the time-to-failure was used as the measure of the kinetic effects. The corrodent was 3-1/2% sodium chloride solution and the pH, dissolved oxygen concentration, and the potential were held constant in each experiment. The specimen surface area exposed to the corrodent was restricted to the notch and the mouth of the crack by masking with an inert coating.

The crack growth rate was independent of K over a wide range. This result suggests that the crack growth may be limited by mass transport, either in the corrodent or in the metal. The crack growth rate was also independent of potential in the deaerated solutions. The cracks exhibited a tendency to branch. Branching was suppressed by side-grooving of the specimen and promoted by cathodic polarization. The branched cracks grew at a much slower rate than the single straight cracks at the same K level. The cracking behavior was interpreted in terms of thermodynamics considerations (Pourbaix diagrams) and kinetic data.



**Thesis**

**"Stress Corrosion Cracking of a High-Strength Steel," Ph.D. Thesis, A. A. Sheinker, to be submitted to the faculty in candidacy for the Ph.D. degree in October 1971**

**Invited Talks**

**"Stress Corrosion Cracking of a High-Strength Steel," A. A. Sheinker and J. D. Wood, ASTM Meeting, Detroit, October, 1971**

Lehigh University

# THE EFFECT OF THICKNESS ON THE STRESS-CORROSION CRACKING KINETICS OF 7039-T66 ALUMINUM ALLOY

J. D. Wood and D. M. Smith

## Objective

This research was directed towards understanding the effects of crack tip stress state on stress-corrosion cracking kinetics in 7039-T66 aluminum alloy plate.

## Approach

The stress-corrosion crack growth rate for a 7039-T66 aluminum alloy in 3-1/2% sodium chloride solution was determined as a function of the stress intensity parameter,  $K$ . Double cantilever beam (DCB) specimens were used under the condition of increasing stress intensity. The thickness of the DCB specimens was varied to determine its effect on the stress-corrosion kinetics.

## Achievements

All specimens regardless of thickness showed a regime in which increases in  $K$  did not produce a corresponding increase in crack growth rate. There was essentially no effect of thickness on the stress-corrosion kinetics at lower  $K$  levels. At high  $K$  levels, there were slightly lower crack-growth rates observed in the thinner-gage specimens. This particular behavior was attributed to the difference in the state of stress ahead of the tip of the crack.

## Publications

"The Effect of Thickness on the Stress Corrosion Kinetics of 7039-T66 Aluminum Alloy," M. S. Thesis, David Smith, February 1970

"The Effects of Stress State on the Stress Corrosion Cracking Kinetics of 7039-T66 Aluminum Plate," David M. Smith and John D. Wood. A preliminary report including work to be contained in a Dissertation to be presented in candidacy for the Ph.D. degree, Lehigh University, June 1970

## Lehigh University

**EFFECT OF CHLORIDE ION CONCENTRATION ON THE STRESS-CORROSION  
CRACKING KINETICS OF Ti-6Al-4V**

J. D. Wood and George S. Hall\*

(\*Graduate Student)

**Objective**

This research attempted to clarify the relationships between two independent variables—crack tip stress intensity and chloride ion concentration—and the stress-corrosion cracking kinetics of a Ti-6Al-4V alloy.

**Approach**

Single edge precracked specimens were cracked in various aqueous concentrations of NaCl. The crack lengths were continuously determined using a crack opening displacement gage and appropriate compliance calibrations.

**Achievements**

The stress-corrosion crack growth rates have been determined as a function of the chloride ion concentration. The relation between crack growth rate and the crack tip stress intensity has the form  $da/dt = AK_I^B$  where  $A$ ,  $t$ , and  $K_I$  are the crack length, time, and stress intensity, respectively. For the chloride ion range investigated,  $B$  is essentially constant (approximately 1/2) and  $A$  varies with concentration. The cracking behavior will be discussed in terms of Beck's electrochemical model.

**Thesis**

"Effect of Chloride Ion Concentration on the Stress Corrosion Cracking Kinetics of Ti-6Al-4V," M. S. Thesis, George Hall, October 1971

**Invited Talks**

Thesis work presented at the Fall Meeting of A.I.M.E., Philadelphia, October 1969

## Lehigh University

## SUBCRITICAL-CRACK GROWTH IN HIGH-STRENGTH STEELS

R. P. Wei and J. D. Landes\*

(\*Graduate Student)

## Objective

The respective roles of deformation and test environment in controlling subcritical crack growth in high-strength steels, and the possible mechanism for environment-induced crack growth are being determined.

## Approach

The kinetics of subcritical-crack growth for a low-alloy, high-strength steel (AISI 4340) in distilled water and in an inert reference environment (dehumidified argon) and companion deformation kinetics are determined. Comparisons between the crack-growth kinetics and the kinetics of deformation and of water-metal reaction will be made through appropriate modeling to develop an understanding of the processes controlling subcritical-crack growth.

## Achievements

The subcritical-crack growth characteristics for an AISI 4340 steel in distilled water and in dehumidified argon have been determined. Companion deformation experiments and model development have been made. The results indicate that subcritical-crack growth can occur in the absence of an aggressive external environment, and the rates of crack growth depend strongly on the crack-tip stress intensity factor,  $K$ . In distilled water, the rates of crack growth approach limiting speeds at high  $K$  levels. The limiting speeds depend on the test temperature and are consistent with an apparent activation energy of 8 to 9 kcal/mole. For crack growth in an "inert" environment, the apparent activation energy is in the range of 11-18 kcal/mole. Creep deformation can and does occur at room temperature, and at mildly elevated temperatures, at stresses commensurate with those near the crack tip. The apparent activation energy for steady-state creep was stress dependent and was in the range of 12 to 18 kcal/mole. Based on comparisons between the apparent activation energies and on model analysis, subcritical-crack growth in an inert environment, under sustained loading, is controlled by deformation at the crack tip.

## Publications

"Correlation between Sustained-Load and Fatigue Crack Growth in High-Strength Steels," R. P. Wei and J. D. Landes, *Materials Research and Standards*, ASTM 9, 25 (1969)

"The Kinetics of Subcritical-Crack Growth under Sustained Loading," J. D. Landes and R. P. Wei (to be published, 1971)

"Kinetics of Subcritical-Crack Growth and Deformation in a High-Strength Steel," J. D. Landes and R. P. Wei (to be published, 1971)

## Thesis

"Kinetics of Subcritical-Crack Growth and Deformation in a High Strength Steel," J. D. Landes, October 1970

## Lehigh University

**EFFECT OF ENVIRONMENT ON SUBCRITICAL-CRACK GROWTH  
IN HIGH STRENGTH METAL ALLOYS**

R. P. Wei, J. D. Landes\*, and S. Hudak\*

(\* Graduate Student)

**Objective**

An understanding is being developed of the influence of atmospheric moisture and water on subcritical crack growth in high strength metal alloys. The relationship between environment-enhanced crack growth under sustained loads and fatigue under cyclic stressing is being examined.

**Approach**

The influences of water and high purity hydrogen and oxygen on the rate of crack growth are examined as functions of the crack-tip stress-intensity factor and test temperature for sustained loading, or fatigue, or both. Specimen thickness and test frequency are used as additional variables when appropriate. The results are analyzed to shed light on the possible mechanisms for environment-enhanced crack growth and to determine possible correlation between sustained load and fatigue-crack growth.

**Achievements**

**Aluminum Alloys.** Fatigue crack growth studies were carried out on 7075-T6 and 7075-T651 aluminum alloys in dehumidified argon, hydrogen, oxygen, and in distilled water over a range of test temperatures. Two test frequencies (5 and 143 cps) and a range of specimen thicknesses were used. Tests in  $D_2O$  at room temperature were also performed. The influence of test frequency on fatigue-crack growth in dehumidified argon was examined for 2024-T3 aluminum as a part of a cooperative program with The Boeing Company. The principal findings of these experiments were (1) Fatigue-crack growth in high strength aluminum alloys is controlled by a thermally-activated process in both inert (argon) and distilled water environments. The apparent activation energy depends strongly on the crack-tip stress intensity factor,  $K$ . (2) The rate controlling process, for crack growth rates below about  $10^{-4}$  inch per cycle, appears to be deformation associated with creating new crack surfaces. (3) From the experimental results and results reported by others, a pressure mechanism of hydrogen embrittlement is inferred. The embrittlement requires the synergistic effect of fatigue and water-metal surface reaction. (4) The influence of specimen thickness on environment sensitivity was demonstrated. The transition in crack-growth rate, attributed to a plane-strain to plane-stress fracture-mode transition, is the result of environmental influences. (5) The rate of fatigue-crack growth in argon is insensitive to test frequency, whereas a mild frequency dependence is noted for tests conducted in distilled water.

**High Strength Steels.** Sustained-load and fatigue-crack growth studies were carried out in distilled water, and in dehumidified argon and hydrogen to complement research initiated by Wei and co-workers at U.S. Steel and other studies elsewhere. H-11, AISI 4340, 18 Ni (250), maraging and 18 Ni (300) maraging steels were used. The

principal findings are: (1) The effect of various environments on crack growth in fatigue are qualitatively the same as those for crack growth under sustained loading. For example, water (liquid or vapor) increases the rate of crack growth both in fatigue and under sustained loads, the severity being dependent on the alloy composition and fracture toughness. Dehumidified hydrogen produces considerably more embrittlement than water vapor; however, the effect of hydrogen is nullified by the introduction of water vapor. The mechanism for environment-enhanced crack growth under both types of loading may then be the same. (2) Fractographic evidence, which shows the fracture paths are the same for fatigue and for sustained loading, tends to support the observation above. Other evidence, which shows that the fracture paths for crack growth in water, or water vapor-containing environment, and in dehumidified hydrogen are different, raises questions regarding "hydrogen embrittlement" as the mechanism for environment-enhanced crack growth in these environments. (3) The rate of fatigue-crack growth for high strength steels in an inert environment is nearly independent of the test frequency. In aggressive environments, it can be quite sensitive to the test frequency depending on the stress-corrosion susceptibility of the material. A prediction procedure for environment-enhanced fatigue-crack growth has been developed and will be discussed below. The influence of gaseous hydrogen on crack growth in a 18 Ni (250) maraging steel is being studied as a function of test temperature. Companion experiments were made on 18 Ni (300) maraging steel and AISI 4340 steel at room temperature. The results indicate that rate limiting speeds were attained in these steels. At room temperature, these speeds were in the range of 0.1 to 0.5 inch per minute. For the 18 Ni (250) maraging steel, the maximum rate-limiting speed occurred at 0 to 25 C; and severe crack branching occurred at temperatures below about -40C.

Correlation between Sustained-Load and Fatigue-Crack Growth. Based on previous observations that the mechanism for environment-enhanced crack growth under sustained loads and in fatigue may be the same, a simple superposition procedure for predicting the rate of fatigue crack growth in an aggressive environment is suggested. In this procedure the rate of fatigue-crack growth in an aggressive environment is considered to be equal to the algebraic sum of the rate of fatigue-crack growth in an inert reference environment and an environmental component, computed from sustained-load growth data and the load profile. This procedure permits characterization of "corrosion fatigue" from two sets of experimental data: (1) fatigue-crack growth data for an inert reference environment, and (2) sustained-load crack growth data in the appropriate aggressive environment. Results with Ti-8Al-1Mo alloy in salt water, H-11 steel, and AISI 4340 steel in distilled water and/or in humid environments, and 18 Ni (250) maraging steel in hydrogen, show that this procedure correctly predicts the influence of test frequency and qualitatively predicts the effect of mean load. Recent results on sustained-load crack growth for AISI 4340 steel in distilled water and other data indicate that the effect of mean load is also quantitatively correct. The procedure is only a first order approximation and does not take account of the "delay phenomenon" for fatigue due to overload, and is applicable only to specific alloy-environment systems. At stress intensity  $K$  levels below the apparent threshold level for stress-corrosion cracking, there appears to be some cooperative effects of fatigue and corrosion, and the proposed superposition procedure should not be applied. The possible mechanism(s) for this interaction are being studied.

#### Publications

"Fatigue-Crack Propagation in a High-Strength Aluminum Alloy," R. P. Wei, Intl. J. Fracture Mech. 4, 159 (1968)

"The Effect of  $D_2O$  on Fatigue-Crack Growth in a 7075-T6 Aluminum Alloy," R. P. Wei and J. D. Landes, Intl. J. Fracture Mech. 5, 69 (1969)

**"Environmental Fatigue in Commercial Aluminum Alloys at Low Stress Intensities,"** J. A. Feeney, J. C. McMillan and R. P. Wei, Boeing Document No. D6-60114, May 1969, available from The Boeing Corporation

**"Application of Fracture Mechanics to Stress Corrosion Cracking Studies,"** R. P. Wei, Proc. Intl. Conf. Fund. Aspects of Stress Corrosion Cracking, 104 (1969)

**"Some Aspects of Environment-Enhanced Fatigue-Crack Growth,"** R. P. Wei, J. Eng. Fracture Mech. 1, 633 (1970)

**"Fracture Mechanics and Corrosion Fatigue,"** A. J. McEvily and R. P. Wei, to be presented at the International Conference on Corrosion Fatigue, University of Connecticut, June 14-18, 1971 and published in the proceedings of the conference

**"Crack Propagation Behavior in Steels,"** J. P. Gallagher and R. P. Wei, to be presented at the International Conference on Corrosion Fatigue, University of Connecticut, June 14-18, 1971 and published in the proceedings of the conference

**"The Influence of Gaseous Hydrogen on Subcritical-Crack Growth in High-Strength Steels,"** R. P. Wei (to be published, 1971)

## Lehigh University

## ENVIRONMENT-ENHANCED FATIGUE

P. C. Faris and R. Bucci\*

(\*Graduate student)

## Objectives

Environment-enhanced fatigue-crack growth in a titanium alloy is being studied as a function of load-time characteristics.

## Approach

Sustained loading and fatigue characteristics of mill-annealed titanium-8Al-1Mo-1V in dry argon, distilled water, and 3.5% salt solution are being measured. Variations in frequency, load profile, and mean load are investigated to determine their effects on fatigue behavior of the alloy in the three environments.

## Achievements

Fatigue results are plotted as the conventional cyclic growth rate,  $da/dN$ , vs. stress intensity amplitude,  $\Delta K$ . In dry argon and in distilled water environments both load profile and frequency effects are slight and the only loading parameter which significantly alters fatigue behavior of the Ti-8-1-1 alloy is mean load. In contrast, Ti-8-1-1 fatigues in a 3.5% salt solution showed a considerable influence of frequency, mean load, and load profile on fatigue behavior. Data accumulated thus far indicates that the rate of fatigue crack growth of Ti-8-1-1 in a salt water system can be represented by the algebraic sum of the rate of fatigue-crack growth in an inert reference environment (dry argon) and an environmental component computed from sustained-load-crack-growth data obtained in salt water. This component is a quantity integrated over one cycle of fatigue loading and incorporates the effects of stress intensity factor variation with time. Environment-enhanced fatigue-crack growth has also been observed to occur at  $K$  levels below  $K_{Isc}$  and work is currently under way to account for this effect.

## Publication and Thesis

"Environment-Enhanced Fatigue in a Titanium Alloy and a Simple Model for the Assessment of Environmental Influence on Fatigue Behavior," R. Bucci, J. Eng. Fracture Mech., forthcoming

"Environment-Enhanced Fatigue in Titanium Alloys," Ph.D. thesis, Robert Bucci, June 1970

## Invited Talks

Talk at ASTM E-24 Subcommittee 4, 1969

ASTM meeting, Philadelphia, March 23-25, 1970



## Lehigh University

**GENERAL FRACTURE MECHANICS****P. C. Paris****Objectives and Achievements**

Articles on various aspects of fracture mechanics are being written for publication.

The major evidence bearing upon subcritical flaw growth in structural materials is reviewed and discussed, and the applicability of fracture mechanics concepts to flaw growth is demonstrated. Environmental cracking under static load, fatigue crack growth, and the combined effects of fatigue and aggressive environments are considered from a fracture mechanics point of view. Finally, engineering applications of the techniques and considerations discussed are indicated.

**Publications**

"Sub-Critical Flaw Growth," H. H. Johnson and P. C. Paris, Eng. Fracture Mech. 1, 1968 p. 3

Lehigh University

**ELASTIC FIELD EQUATIONS FOR BLUNT CRACKS****P. C. Paris and M. Creager\***

(\*Graduate Student)

**Objective**

The elastic stress field equations for blunt cracks were derived and employed in analyzing a dissolution model for the arrest of stress-corrosion cracks by crack tip blunting.

**Approach**

Pertinent equations were developed and tabulated. The equations were employed in analyzing possible models for crack arrest in stress-corrosion cracks.

**Achievements**

The elastic stress field equations for blunt cracks were presented in a form equivalent to the usual sharp crack tip stress fields for each of the three loading modes. When these elastic stress field equations are incorporated into a stress-corrosion cracking model based upon material dissolution, indications are that for accelerated stress-corrosion cracking to occur the dissolution velocity should be more strongly dependent upon stress than a one-half power law. The relationship of dissolution velocity to stress is equally correct if there is a plastic zone in the vicinity of the crack tip, and therefore it may represent a "minimum criterion" for stress-corrosion cracking with material dissolution. The stress field equations presented have other applications as well.

**Thesis**

"The Elastic Stress Field Near the Tip of a Blunt Crack," M. Creager, M.S. Thesis, October 1966

## Lehigh University

## STRESS-CORROSION MODELS

P. C. Paris and M. Creager\*

(\*Graduate Student)

## Objective

Theoretical models of stress corrosion at a macroscopic level were developed and investigated. Results were compared to experimental data generated elsewhere.

## Approach

General models which involve changes in elastic constant, or which involve changes in maximum supportable stress were studied. Particular models of stress corrosion were then developed and the boundary value problems which arose were studied. A particular model having bulk diffusion as the rate-controlling process was investigated in detail and comparisons were made with the stress-corrosion behavior of steel and glass in water environments. The boundary-value problems describe the stress distribution in an infinite bi-material parabolic cylinder and the stress-assisted diffusion from the surface of a growing blunt crack.

## Achievements

Some general descriptive models of stress corrosion in which the bulk material is treated as a continuum were derived with no assumptions being made as to rate-controlling processes. Various diffusion or reaction processes were subsequently considered. The stress distribution in an infinite bi-material parabolic cylinder, subjected to anti-plane loads on the free surface was found in closed form. The solution to the associated in-plane load problem was determined by the numerical solution of two coupled first-order ordinary differential equations. Using a modified form of Fick's law which includes the effect of a stress field, some concentration distributions were determined for the problem of diffusion from the surface of a growing blunt crack. For the diffusion model used and over the range of parameters investigated, the velocity of crack growth and the stress intensity factor are the most important parameters affecting the distribution of concentration of the diffusion species. The crack-tip radius is a less important parameter than either the stress intensity factor or the velocity. Stress-corrosion models which are based upon bulk diffusion as the rate-controlling process must consider the effects of both the stress intensity factor and the velocity of crack growth on the diffusion process itself. The model in which bulk diffusion of a damaging species is considered as the rate-controlling process describes the general character of the relationship between crack-growth velocity and stress-intensity factor as found experimentally for both glass and steel in water. Additional understanding of diffusion phenomena in the crack tip vicinity is necessary to describe clearly the role of hydrogen in stress corrosion of steels.

## Thesis

"Stress Corrosion Models and Some Associated Boundary Value Problems,"  
M. Creager, Ph.D. Thesis, Lehigh University, 1969

Lchigh University

**STRESS-CORROSION CRACKING IN THE COPPER-GOLD SYSTEM**

R. Bakish

**Objective**

Information relating to the effect of composition on the kinetics of cracking of copper-gold alloys was determined.

**Approach**

As-cast and homogenized specimens of Cu-Au alloys containing 97, 70, 50, 40, 35, and 25 wt-% copper were subjected to immersion tests in 2%  $\text{FeCl}_3$  aqueous solution at room temperature and at  $100^\circ\text{C}$  for from 2 hours to 12 days. All tests were repeated using specimens which differed from the above only in having been plastically deformed by indentation. Specimens were examined metallographically after immersion, and their ductility was tested by indentation.

**Achievements**

After treatment at  $100^\circ$ , 97% copper alloys suffered general dissolution. Intermediate composition alloys showed copper leaching and oxidation within the alloy, accompanied by loss of ductility. Low copper content alloys were not attacked. After treatment at room temperature, the most consequential loss of strength was shown to take place with 70:30 and 50:50 alloys. General attack of the 97:3 alloy was observed, but embrittlement was lacking. The 60:40 alloy also did not show embrittlement although the reason for this behavior is not at all clear. No changes in behavior as a result of pre-indentation could be determined.

## Lehigh University

## STRAIN ELECTROMETRY OF ALUMINUM

H. Leidheiser, Jr., and E. Kellerman

## Objective

The potential changes of aluminum wires in various electrolytes were observed after abrupt straining, and the effects of changing experimental parameters relating to stress-corrosion cracking problems were determined.

## Approach

Annealed commercially pure aluminum wires immersed in sodium chloride solution or other electrolytes were abruptly strained 1.5-12%. The potential before straining and the changes in potential for one or more seconds after strain were recorded. Studies were made of the effects of varying the pH, altering the oxygen content of the solution, changing the anion or cation of the electrolyte, and anodizing or boiling the wires before stretching.

## Achievements

The maximum potential achieved after straining in 0.1 M NaCl solution decreased with decrease in pH, but the rate of decay to the initial steady state value (-0.66v) was independent of pH over the range of 1.5 to 6.5. In deaerated solutions, decay to within 100 mv of the steady-state value occurred in less than 120 seconds, while in the presence of oxygen decay occurred much more rapidly. The oxygen content of the solution did not affect the initial portions of the potential-time curve. Increasing the amount of strain up to 6% increased the maximum potential. Above 6% strain the potential remained constant at  $V_{max}$  for periods of time which increased with increase in total strain. Boiling the wires before straining decreased the potential changes observed; the curves obtained at large strain were similar to the curves obtained at small strain with non-boiled wires. Anodizing the wires caused curves subjected to moderate strain to have the appearance of curves obtained at large strain with reference wires. Curves measured in NaCl,  $\text{Na}_2\text{SO}_4$ , sodium tartrate, and  $\text{Na}_2\text{Cr}_2\text{O}_7$  solutions of equal ionic strength were similar under conditions of similar pretreatment of the wire. The following metallic cations were added in concentrations up to 1 M: aluminum, sodium, magnesium, zinc, cadmium, nickel, iron, lead and copper. Copper, above .01 M, and lead and iron at the highest concentrations reacted with the aluminum wire. Aluminum, sodium, and magnesium ions had little effect on the decay curves. For other added ions, the maximum potential change was decreased greatly, and plateau regions were observed in the decay portions of the curve. No change in the pH of the solution close to the wire could be determined. High purity aluminum wire gave standard strain electrometry curves very similar to those obtained with the commercially pure materials. An annealed 7075 alloy (T6 could not be strained as required for these experiments) gave a much smaller potential anodic shift after strain (400 mv at pH 5.5 compared to 900-1000 mv for the commercially pure aluminum).

## Publications

"Strain Electrometry Studies of Aluminum," H. Leidheiser, Jr., and E. Kellerman, *Corrosion* 26, 1970, p.99

**Invited Talks**

**"Basic Studies of Surface Phenomena and Their Relation to Corrosion", Henry Leidheiser, Jr., presented at ASTM meeting, Atlanta, Georgia, October 4, 1968**

**"Electrochemical Studies of Stress Corrosion Cracking of Aluminum Utilizing Strain Electrometry and Synthetic Cracks," H. Leidheiser, Jr., E. Kellerman, and V. V. Subba Rao, Presented at NACE Symposium on Fundamental Corrosion Research in Progress, Houston, March 1969**

## Lehigh University

## FERROMAGNETIC STUDIES OF NICKEL

M. M. P. Janssen

## Objective

The nature of the compressive stresses in thin nickel films deposited in UHV was studied. The amount and mechanisms of stress relief caused by gas adsorption on the films were investigated.

## Approach

Thin nickel films were deposited at room temperature at better than  $5 \times 10^{-10}$  torr onto glass substrates. Ferromagnetic measurements on the films before and after admission of gases to the system were used to study the compressive stresses in the films and their relief upon admission of gas.

## Achievements

Oxygen adsorption on clean films resulted in essentially complete stress relief.  $N_2O$  had the same effect indicating it decomposed on the Ni surface to nitrogen and oxygen.  $N_2$  had no effect on the surface free energy, but  $\gamma_{Ni}$  was changed from 2500 dyne/cm to 200-500 dyne/cm in partial stress relief by CO,  $H_2$ ,  $H_2O$  or pyridine, and then to less than 100 dyne/cm by  $O_2$ ,  $N_2O$  or air. Films less than 100 Å thick were shown to have an island structure. Annealing thicker films at 250°C for 20 minutes resulted in apparent stress release.  $O_2$  adsorption produced the same stress relief resonance shifts with either annealed or unannealed films. This last observation, coupled with the fact that for about 500 Å thick films 250°C is a good annealing temperature, is excellent evidence for the correctness of a surface tension model for the observed compressive stress. Any other form of stress would be removed by annealing.

## Publications

"Release of Compressive Intrinsic Stress in Ultraclean Thin Nickel Films as a Result of Adsorption of Gases, "M. M. P. Janssen, J. Appl. Phys. 40, 1969, p. 3055

"FMR Study of Surface Tension Related Stress Effects in Ultraclean Nickel Thin Films, " M. M. P. Janssen, J. Appl. Phys. 41, 1970, p. 384

"Observation of Spin Wave Resonance in Nickel Thin Films after Adsorption of Oxygen, "M. M. P. Janssen, J. Appl. Phys. 41, 1970, p. 399

## Lehigh University

## CREVICE CORROSION OF ALUMINUM

H. Leidheiser, Jr., and V. V. Subba Rao

## Objective

Potential differences between the sides and tip of a synthetic crack were investigated under a variety of conditions thought to relate to the conditions existing during crack propagation in stress-corrosion cracking experiments.

## Approach

Synthetic cracks were constructed by sandwiching aluminum between glass cover slides. Two pieces of aluminum, not in electrical contact, were used, one corresponding to the base of the crack and another corresponding to the side of the crack. In some cases the aluminum corresponding to the base of the crack was a wire which could be stretched externally. Potential differences between the two pieces of aluminum were measured in sodium chloride solution as described below.

## Achievements

The more interesting results are: 1) After several days the base of the crack became anodic to the side of the crack, probably reflecting the formation of an oxygen concentration cell with the base of the crack being oxygen-deficient. 2) Additions of acid to the base of the crack with a hypodermic needle caused the base to become anodic with respect to the side of the crack. The potential difference decayed over 24 hours when the acid became distributed evenly throughout the crack by diffusion and convection. 3) Addition of aluminum ions to the base of the crack made the base anodic to the side of the crack. 4) Straining the wire corresponding to the base of the crack caused an immediate and large anodic shift in the potential of the wire. In some cases the base of the crack remained significantly anodic to the side of the crack for several days after straining; in others, the potential difference tended towards zero after 24 hours.

## Invited Talks

"Electrochemical Studies of Stress Corrosion Cracking of Aluminum Utilizing Strain Electrometry and Synthetic Cracks," H. Leidheiser, Jr., E. Kellerman, and V. V. Subba Rao, Presented at NACE Symposium on Fundamental Corrosion Research in Progress, Houston, March 1969.



## Lehigh University

## FERROMAGNETIC STUDIES OF IRON THIN FILMS

H. Leidheiser, Jr., and R. Kellerman\*

(\*Graduate student)

## Objective

Studies are being made to determine the applicability of ferromagnetic resonance techniques to investigations of the interaction between clean iron surfaces and various gases.

## Approach

The basic techniques of depositing a metal film in ultrahigh vacuum and observing its ferromagnetic resonance spectrum follow the nickel work done in this laboratory by Janssen (see his report). Iron, however, presents both physical and chemical problems not associated with nickel. In particular the very high demagnetizing field of iron has necessitated modification of the spectrometer to increase the magnetic field strength, and the very high chemical reactivity of iron has demanded rather elaborate cleaning techniques be applied to the iron wire from which the films are evaporated.

## Achievements

A UHV apparatus, adapted for rigorous cleaning of the iron wire before evaporation of a thin film, has been constructed. The position of the ferromagnetic resonance is a function of film thickness for clean films; these observations are not in accord with published information. Multiple-line resonances have been observed with very thin films. The explanation for this observation is still being sought.

Changes in the position of the ferromagnetic resonance occur upon admission of either oxygen or hydrogen. Hydrogen gas, in the pressure range of  $10^{-8}$  to  $10^{-7}$  torr, causes a small irreversible and a larger reversible change in the resonance field upon varying the gas pressure. This observation is in accord with what is presently known about chemisorption in the iron-hydrogen system.

Radiotracer studies of adsorption on the very thin films are being carried out in an attempt to gain information about the morphology of these films.

## Invited Talks

"Studies of Iron Surfaces Using Ferromagnetic Resonance," Henry Leidheiser, Jr., and Richard Kellerman, 44th National Colloid Symposium, Lehigh University, June 22, 1970.

"Ferromagnetic Resonance Techniques as a Means for Studying Chemisorption," Henry Leidheiser, Jr., Gordon Conference on Corrosion, July 27, 1971.

Lehigh University

## CHEMISORPTION ON CLEAN METAL SURFACES

K. Klier

## Objective

Interactions of carbon monoxide with bulk and single crystal metal surfaces have been studied to determine the structure, equilibria, and rates of surface reactions in adsorbed layers.

## Approach

$^{14}\text{C}$ -labeled carbon monoxide is adsorbed on UHV-cleaned metal surfaces. The measured quantities are: equilibrium amounts adsorbed, effective molecular cross sections at saturation, collision efficiencies ("sticking probabilities"), and the rates of exchange reactions between adsorbate and gas. Derived quantities are: heat of chemisorption (binding energy), lateral interaction energy, mobility, chemical potential, and actual molecular cross sections in the adsorbed state. A statistical mechanical theory developed by the author permits the determination of these quantities.

## Achievements

The measurement of  $^{14}\text{C}$  on small surfaces has been performed at pressures from  $1 \times 10^{-10}$  torr up, with a sensitivity of detecting adsorbates on areas of  $0.1 \text{ mm}^2$ . The method is readily applicable to systems containing any organic adsorbate. Under the UHV conditions employed, metal surfaces studied remain clean (if made clean by ion and electron bombardments) and exhibit reproducible properties. The instrument used contains a UHV Geiger counter. On nickel single crystal planes of (100) and (110) orientation, the following results were obtained: The full description of state ( $p$ ,  $V$ ,  $T$ ) was determined for the systems carbon monoxide plus (100) nickel and (110) nickel between 200 and  $300^\circ \text{K}$  and  $10^{-9}$  -  $10^{-1}$  torr. The effective molecular cross section of carbon monoxide on single crystal nickel surfaces was found to be  $9 \text{ \AA}^2$ . The rates of adsorption and exchange were measured over a wide range of pressures and interpreted by a statistical mechanical theory which permitted three conclusions: 1) The binding energy of carbon monoxide on both planes is 25-26 kcal/mole, and the lateral interaction energy is of the order of 2-3 kcal/mole; 2) the adsorbate is mobile, and its chemical potential sharply rises at coverages of  $9 - 11 \times 10^{14}$  molecules/ $\text{cm}^2$ , leading to extremely fast exchange between adsorbed and gaseous carbon monoxide molecules; and 3) the adsorbate is uniform if the crystal planes are clean and well annealed. If the crystal planes are chemically clean but geometrically rough, the adsorbate is heterogeneous, and its binding energies range probably from 40 kcal/mole to 25 kcal/mole. If the crystal planes are covered by chemisorbed oxygen or surface oxide, the chemisorption of carbon monoxide is reduced by approximately two orders of magnitude. The theory of adsorption and exchange rates also quantitatively explains the adsorption equilibria. Clean surfaces behave differently if they are atomically smooth or if they are rough. The adsorbate on rough surfaces is tightly bound and fixed while the adsorbate on smooth surfaces is weakly bound and mobile. This may be of some importance to stress-corrosion cracking in that the chance for weak chemisorption in cracks will increase if the crack surface can be made smooth by some annealing procedure. On bulk polycrystalline iron and iron single crystal planes of (111), (110), and (100) orientation the behavior of rough iron surfaces is similar to that of nickel. On

smooth iron surfaces, no matter whether in single crystal or polycrystalline form, carbon monoxide chemisorption saturates at about 10% of the saturation value for nickel, and the sticking probabilities are generally very low. This may be an ultimate manifestation of the relative inertness of smooth surfaces but may also be due to some undetected contamination of the iron surface. Great care was taken to avoid carbon, oxygen, and water contamination. Some of the iron surfaces were cleaned for hours by argon bombardment in UHV, but their "inertness" towards CO after temperature annealing did not change. Work is continuing on maraging steels.

#### Publications

"A Geiger-Muller Counter for Ultrahigh Vacuum Systems," K. Klier, Rev. Scientific Inst. 40, 1969, p. 372

"Chemisorption of Carbon Monoxide on (110) and (100) Nickel Crystal Faces," K. Klier, A. C. Zettlemoyer and H. Leidheiser, Jr., J. Chem. Phys. 52, 1970, pp. 589-602.

#### Invited Talks

"Interaction of Carbon Monoxide with Clean Nickel Surfaces," K. Klier and A. C. Zettlemoyer, presented at 156th National ACS Meeting, Atlantic City, Sept. 1968

"Exchange Reactions at Interfaces," invited lecture at Dept. of Chemistry, The Johns Hopkins University, Nov. 1968

"Radiotracer Studies of Adsorption on Ultraclean Surfaces," Kamil Klier, Gordon Conference on Corrosion, July 1969

"Adsorption of Carbon Monoxide on Iron Using Radiotracer Techniques," Kamil Klier, 44th National Colloid Symposium, June 22, 1970

## Lehigh University

## RARE GAS (ARGON) ION BOMBARDMENT

R. Coughlin, H. Leidheiser, Jr., and E. Chornet\*

(\*Graduate Student)

## Objective

The binding energies and ion-sticking probabilities of argon atoms on nickel, iron, and titanium are being studied.

## Approach

Argon atoms, previously incorporated in a wire as a result of ion bombardment, were thermally released by a 2 to 10 second flash. Ultrahigh vacuum conditions (less than  $3 \times 10^{-10}$  torr), a hot tungsten filament and molybdenum grid bombarding unit, a Bayard-Alpert ionization gauge pressure sensor, and a quadrupole residual gas analyzer were used. The polycrystalline specimens were chemically polished, sealed into the vacuum system, and degassed thoroughly until the pressure in the system with the wire hot could be maintained in the  $10^{-10}$  torr range. Maximum degassing temperatures were: nickel,  $1000^{\circ}\text{C}$ ; iron,  $875^{\circ}\text{C}$ ; titanium,  $900^{\circ}\text{C}$ . The wires were ion bombarded in 5 minute intervals. Each bombardment was followed by a 30-minute annealing period, and the total bombarding time before any flash was about 1 hour. Nickel and iron were also reduced and decarburized by heating specimens in hydrogen at temperatures between  $600^{\circ}$  and  $800^{\circ}$  during two cycles of 16 hours each.

## Achievements

For nickel the number of impinging ions ranged from  $3 \times 10^{13}$  to  $10^{17}$  ions/cm<sup>2</sup>, that of desorbing argon atoms from  $2 \times 10^{12}$  to  $10^{14}$  atoms/cm<sup>2</sup> from which the sticking probability of argon on nickel was obtained. The pressure spectra on raising the wire temperature revealed six different peaks for a high number (more than  $10^{16}$  ions/cm<sup>2</sup>) of incident ions and only three distinct peaks at  $10^{14}$  ions/cm<sup>2</sup> or less. The energies of the binding states (peaks) are being calculated. On titanium, experiments with a high number of incident ions were carried out. The presence of three binding states was observed. Analysis of the first two peaks showed energies of 32 and 56 kcal/mole. The third peak, of a higher energy, is poorly resolved and did not allow quantitative estimation. For iron, only one peak has been found although the cleaning procedure has not yet been completed. The nickel calculations will be continued, a complete set of iron experiments will be performed, and the titanium behavior at a low incident number of ions will be studied.

## Invited Talks

"Flash Desorption of Argon Imbedded Within Iron, Nickel and Titanium," E. Chornet, R. N. Coughlin, and Henry Leidheiser, Jr., 44th National Colloid Symposium, Lehigh University, June 22, 1970

## Lehigh University

## FLASH FILAMENT STUDIES

R. Goughlin, H. Leikheiser, Jr., and E. Chornet\*

(\*Graduate student)

## Objective

A comparative study of the chemisorption of hydrogen on clean surfaces of nickel, iron and titanium, with extension to the methanol-titanium system, has been carried out.

## Approach

The flash filament technique gives information concerning the rates of adsorption and desorption, and the nature and binding energies of the adsorbed species.

## Achievements

Sorption and desorption rates and sorption equilibria of hydrogen have been investigated on polycrystalline filaments of nickel, iron, and titanium under ultrahigh vacuum conditions using the flash desorption technique. The wires were cleaned by argon-ion bombardment followed by heating.

On nickel, hydrogen atoms exist on the surface at 298°K. as a single phase. The dissociated hydrogen recombines upon desorption with a constant activation energy of 17.5 kcal/mole up to the maximum coverage explored,  $0.5 \times 10^{15}$  atoms/cm<sup>2</sup>. A low sticking probability of  $3 \times 10^{-3}$  was explained by the presence of a weakly-bonded precursor state.

A single phase of adsorbed hydrogen atoms was also found on iron. Desorption follows a second-order reaction with an activation energy of 20.3 kcal/mole, which value remains constant up to  $0.2 \times 10^{15}$  atoms/cm<sup>2</sup> and then decreases with further coverage. Entropy calculations indicate that the adsorbate is mobile and its behavior approaches that of an ideal two-dimensional gas. The initial rates of adsorption are explained in terms of an activated complex, molecular in nature, which loses rotational freedom with respect to the gas phase and requires about 0.5 kcal/mole to dissociate. Lateral interactions are included in the interpretation.

On both nickel and iron, a second, small desorption peak appears at high temperatures at long exposure times, suggesting diffusion of hydrogen into the interior.

Hydrogen readily penetrates titanium at room temperature; the penetration is appreciable at 130°K. Sorption at 400°K. and higher temperatures follows the solubility laws of hydrogen in titanium. Two distinct peaks were found upon desorption. The peak at 100°K. is consistent with a first-order reaction with an activation energy of 4 kcal/mole. A second broad peak at higher temperatures is indicative of both surface and bulk hydrogen. At 298°K. and lower temperatures, the sorption rate is a linear function of pressure.

The initial heats of adsorption of hydrogen on nickel, iron, and titanium are consistently lower than values reported by other workers who used evaporated films. The low and nearly constant heats of adsorption are a characteristic of the clean and smooth surfaces used in this work.

When a clean titanium surface is exposed to methanol, hydrogen penetrates into titanium. Upon flashing, there is a violent reaction accompanied by a substantial decrease in the amount of carbon monoxide as determined mass spectrometrically. This reaction contaminates the surface and subsequent adsorption of hydrogen proceeds at a much lower rate than in the case of a fresh surface.

Pretreatment of metal wires by argon-ion bombardment, followed by annealing, produces a clean reproducible surface on nickel, iron, and titanium. Small quantities of carbon monoxide in the gas phase ( $5 \times 10^{-9}$  torr partial pressure) results in contamination of the surfaces during argon-ion bombardment as judged from the negligible amounts of hydrogen adsorbed. Hydrogen chemisorption provides a useful criterion of cleanliness of a surface.

#### Thesis

"Flash Desorption of Hydrogen on Clean Nickel, Iron and Titanium Wires,"  
Esteban Chornet, Ph.D. Thesis, Lehigh University, submitted to the faculty for action, June 1971

## Lehigh University

**"**MÖSSBAUER SPECTROSCOPY OF SURFACES

H. Leidheiser, Jr., G. W. Simmons, and E. Kellerman

## Objectives

The purpose of this study is to determine the applicability of Mössbauer Spectroscopy to analysis of very thin surface films on iron and steels.

## Achievements

Mössbauer spectroscopy is a form of resonance spectroscopy involving gamma-rays with energies of 10-100 keV. The iron isotope, Fe-57, present in natural iron to the extent of approximately 2%, is a Mössbauer-active species and resonantly absorbs the 14.4 keV gamma-ray emitted by the activated state of Fe-57. Information about the chemical environment of an iron atom and its magnetic properties can be obtained from such experimental parameters as the chemical shift, quadrupole split, the magnetic hyperfine splitting, and the superparamagnetic characteristics.

Techniques have been developed for improving the applicability of Mössbauer spectroscopy to the study of iron surfaces. The K-conversion and Auger electrons which are emitted following resonance absorption of the 14.4 keV incident gamma-ray are detected in 2- $\pi$  geometry. Further enhancement of the sensitivity for detection of species at the surface is made by enrichment of the surface of the sample with electro-deposited Fe-57.

The passive film on iron, 15-50 Å in thickness, formed by immersion in sodium nitrite solution or by anodic treatment in sulfuric acid or borate electrolytes, is readily studied by the electron-detection technique. The experimental results obtained to date suggest that the major component in the passive film on iron is gamma-Fe<sub>2</sub>O<sub>3</sub>. The thinner films exhibit superparamagnetic behavior whereas the thicker films show magnetic hyperfine splitting.

Mössbauer spectroscopy is proving to be a powerful tool for surface studies of iron and steel.

## Invited Talks

"Studies of Surfaces Using Mössbauer Spectroscopy," H. Leidheiser, Jr., First Conference on Colloid and Surface Chemistry, Hungarian Academy of Sciences, Matrafüred, Hungary, May 24, 1971

"Mössbauer Spectroscopy of the Passive Film on Iron," Gary W. Simmons, Elsie Kellerman, and Henry Leidheiser, Jr., to be presented at meeting of the Electrochemical Society, Cleveland, October, 1971

Lehigh University

## HYDROGEN ABSORPTION BY ALUMINUM

H. Leidheiser, Jr., and N. Das\*

(\*Graduate student)

## Objective

The hydrogen which passes into aluminum during reaction with various aqueous solutions is being determined. Correlations between hydrogen dissolution and stress-corrosion cracking and fatigue properties are being sought.

## Approach

Vacuum extraction at 600°C and  $10^{-6}$  torr is used to measure the amount of hydrogen present in aluminum after exposure to aqueous solutions at 60° and 100°. After vacuum treatment, aluminum samples with various surface/volume ratios are exposed to water for several minutes to 24 hours. The hydrated oxide formed during corrosion is removed with a chromic acid-phosphoric acid solution before extraction. Differentiation between the hydrogen formed as a consequence of reaction with water and the hydrogen formed by the reaction of the hydrated film with aluminum during extraction is made by appropriate use of  $D_2O$  and  $H_2O$  in formulating the reactive solutions. The extracted gas is then analyzed mass spectrometrically.

## Achievements

The total amount of hydrogen which penetrates into aluminum during reaction with water at 100° is linearly related to the surface area. A typical result for a sample exposed to pure water for 24 hours at 100° is 0.00017 ml./cm<sup>2</sup>. For this particular sample, the total amount of hydrogen is equivalent to 0.056 ml./100 g. of aluminum.



**Lehigh University****REVIEW OF THE ALUMINUM-HYDROGEN SYSTEM**

**R. D. Iyengar and H. Leidheiser, Jr.**

**Objective**

A review of the literature concerning the aluminum-hydrogen system was prepared.

**Achievements**

Published data for the aluminum-hydrogen system were reviewed. The adsorption of hydrogen on aluminum and the effect thereon of the oxide layer were considered. In addition, reports of the diffusion of hydrogen in aluminum and of the solubility of hydrogen in aluminum and its alloys were listed and discussed.

**Publication**

"The Aluminum-Hydrogen System: A Review", R. D. Iyengar and H. Leidheiser, Jr., report distributed to ARPA participants.

Lehigh University

## REVIEW OF HYDROGEN IN IRON

H. Leidheiser, Jr., and E. Kellerman

### Objective

An annotated bibliography of the literature concerning the effect of environment on the diffusion of hydrogen in iron and steel is being prepared.

### Achievements

Published data for the diffusion of hydrogen in iron were surveyed. Reports in the literature of the effect of solution composition on the penetration of electrolytically generated hydrogen into iron and steel were collected.

## Lehigh University

## THE FRACTURE OF MICA

P. C. Paris and R. Leonesio\*

(\*Graduate Student)

## Objective

The influence of moisture on the fracture energy of mica crystals is being studied.

## Approach

The use of double cantilever beam specimens permits the fracture energy of uniformly thick mica crystals to be determined from  $G = 3 \Delta^2 / 2bKL^4$  where  $G$  is the splitting energy in ergs/cm<sup>2</sup>,  $\Delta$  is the total displacement of the ends of the beam,  $L$  is the crack length,  $b$  is the width of the specimen, and  $K$  is a constant representing the elastic stiffness of the beams. The value of  $K$  varies from specimen to specimen and is found experimentally for each specimen used. Muscovite mica was split in water, in air with varying humidity, in helium with varying humidity, and in dry helium. The crack tip was located with a travelling microscope, and  $\Delta$  was measured with another microscope. The water experiments were done by immersing the bottom of the specimen so that the water surface was above the crack tip. The experiments at various relative humidities were done in a glass chamber. Varying amounts of moisture were introduced by heating the bulb. The dew points of the gas leaving the chamber was measured with a dew point hygrometer, and the relative humidity was then calculated from the corresponding vapor pressures. Zero humidity conditions were reached by first baking the system at 200°C for at least one hour under mechanical pump vacuum, and then passing high purity helium through a liquid nitrogen cold trap and into the chamber.

## Achievements

The fracture energy of mica in water varied between 150 and 250 ergs/cm<sup>2</sup> for the several specimens tested. This energy is virtually independent of crack velocity from 0.1 micro-inch/sec to 10,000 micro/inches/sec. When tested as a function of relative humidity in both helium and air, the fracture energy varied uniformly from 350 ergs/cm<sup>2</sup> at 100% relative humidity to 600 ergs/cm<sup>2</sup> at 2 to 5% relative humidity. Further testing is being done to determine any shift in energy with a change in temperature. Below 5% relative humidity and especially at 0% relative humidity the data points showed much scatter. Values for the fracture energy varied from 600 ergs/cm<sup>2</sup> to 3,000 ergs/cm<sup>2</sup> at atmospheric pressure and room temperature, and from 1,000 ergs/cm<sup>2</sup> to 14,000 ergs/cm<sup>2</sup> in a vacuum of about 10<sup>-2</sup> mm. of mercury. These results indicate that for very low humidity the fracture energy of mica is strongly dependent on impurities within the system. A unique feature which mica possesses is its ability to reheel itself upon load release. The crystal can then be resplit and a new fracture energy measured. For mica resplit in water and in moist helium or air, the energy for refracturing is always lower than that of the original fracture. This is to be expected because adsorbed moisture trapped between resealed layers will lower the energy needed for the second fracture. In a dry environment in many cases the energy for resplitting was found to be greater than the

original fracture energy. This phenomenon was observed in environments of air, helium, hydrogen, and carbon dioxide, and also under mechanical pump vacuum. That the energies for refracturing were sometimes two or three times higher than the original fracture energy was totally unexpected and is as yet unexplained.

#### Thesis

"Environmental Effects on the Fracture of Mica Crystals," Robert B. Leonesio, Ph.D. Thesis, June 1970

## Lehigh University

**GLASS CRACKING**

E. Sommer and G. Irwin

**Objective**

New apparatus, experimental techniques, and mathematical methods of analysis applicable to fracture mechanics studies of glass were investigated.

**Approach**

An apparatus was designed and constructed for propagating cracks in glass, and an interference method was developed whereby the opening displacement of the cracks can be accurately and simply determined. Experimental results were compared to analytical predictions.

**Achievements**

Using a travelling microscope mounted on an optical bench associated with an eccentric loading apparatus, simple measurements of the interference fringes produced by monochromatic illumination of a crack tip were used to determine accurately the opening displacement of cracks in glass. Some studies of plastics were also attempted. Results of glass cracking under eccentric tension load were compared with analytical prediction from the boundary collection method and from Westergaard analysis as detailed in the second publication listed below. Additionally, since the crack opening displacement is analytically related to the stress intensity factor,  $K$ , a  $K$ -calibration curve for the crack-line-loaded, single-edge notched plate was established. Finally an original method for crack initiation in glass was investigated.

**Publications**

"A Remark on Crack Initiation in Glass Plates," E. Sommer, Eng. Fracture Mech., to be published.

"An Optical Method for Determining the Crack-Tip Stress Intensity Factor," E. Sommer, Eng. Fracture Mech., to be published.

Lehigh University

**RUTILE STUDIES BY ELECTRON SPIN RESONANCE****R. D. Iyengar****Objective**

Further characterizations of the oxygen species produced by oxidation of outgassed rutile powders were made.

**Approach**

Standard ESR techniques were used to determine spectra of powdered rutile samples which had been outgassed and then treated with oxides of nitrogen under various conditions.

**Achievements**

Nitrogen dioxide restored the oxygen deficiency at the surface of outgassed rutile, and produced a signal which has been attributed to  $O_2^+$ . Nitrous oxide reacted with rutile to produce the same signal. Neither oxide of nitrogen produced  $O_2^-$  on interaction with vacuum-outgassed high-area rutile.

**Publications**

"An ESR Study of the Nature of the Surface Oxygen During Oxidation of a Non-stoichiometric Rutile Surface with Oxides of Nitrogen," R. D. Iyengar, M. Codell and J. Turkevich, *J. Catalysis* **9**, 1967, p. 305

## Lehigh University

## ELECTRON SPIN RESONANCES STUDIES OF ZINC OXIDE

R. D. Iyengar and V. V. Subba Rao

## Objective

Identification of the chemical species formed by surface interaction of zinc oxide with oxygen, chlorine, nitrobenzene, oxides of nitrogen, and tertiary butyl hydroperoxide was sought.

## Approach

Electron spin resonance spectra were recorded after treatment of vacuum-outgassed ZnO with  $\text{NO}_2$ , NO,  $\text{N}_2\text{O}$ ,  $\text{O}_2$ ,  $\text{Cl}_2$ , nitrobenzene, and tertiary butyl hydroperoxide. From variations in the spectra with further treatments such as outgassing, heating and/or cooling, as well as from power variation studies, the ESR results were correlated with species formed on the oxide surface.

## Achievements

Both  $\text{NO}_2$  and NO were found to be adsorbed as rigid neutral molecules. Confirmation of the assignment was provided by the use of the two adsorbates enriched in  $^{15}\text{N}$ . The origin and identity of the signals produced by  $\text{N}_2\text{O}$ , NO, or  $\text{Cl}_2$  were investigated, but no final conclusions concerning the species involved could be reached. Nitrobenzene on the oxide surface was converted to the anion radical. With tertiary butyl hydroperoxide two signals are formed which can be understood in terms of oxygen ion vacancies and interstitial zinc ions.

## Publications

"Electron Spin Resonance of Nitrogen Dioxide ( $\text{NO}_2$ ) Adsorbed on Zinc Oxide," R. D. Iyengar and V. V. Subba Rao, J. Am. Chem. Soc. 90, 1968, p. 3267

"ESR Studies of the Interaction of  $\text{O}_2$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}$  and  $\text{Cl}_2$  with Zinc Oxide," R. D. Iyengar, V. V. Subba Rao and A. C. Zettlemoyer, Surface Science 13, 1969, p. 251

"An ESR Investigation of Nitrobenzene Adsorbed on Zinc Oxide," V. V. Subba Rao, R. D. Iyengar, and A. C. Zettlemoyer, J. Catalysis 12, 1968, p. 278

"Electron Spin Resonance Study of Hydroperoxide on Zinc Oxide," M. Codell, H. Gisser, J. Weisberg, and R. D. Iyengar, J. Phys. Chem. 72, 1968, p. 2460

## Lehigh University

## ELECTRON SPIN RESONANCE STUDIES OF TITANIUM DIOXIDE

R. D. Iyengar and R. Kellerman\*

(\*Graduate Student)

## Objective

Identification of the source of two of the more frequently observed ESR signals from oxygen-treated rutile and anatase was sought.

## Approach

Standard ESR techniques including determinations of hyperfine splitting and isotopic substitution were employed. Sample pretreatments (e.g., outgassing and oxygen exposure) were varied, and the source and preparation method of the samples (ammonia-precipitated  $\text{TiO}_2$  was compared to other types of  $\text{TiO}_2$ ) were changed to determine the cause of the observed signals.

## Achievements

The two signals were shown to be due to impurity centers. Final identification of these centers was not made, but by a comparison of the known hyperfine splitting associated with the  $^{14}\text{N}$  nucleus and the change in the spectrum when  $^{14}\text{N}$  was replaced by  $^{15}\text{N}$ , they were shown to involve nitrogen. The origin of the nitrogen impurity was established as being the ammonia precipitation stage of rutile manufacture.

## Publications

"Formation and Nature of Radical Species in the Oxidation of Precipitated Titanium Dioxide," R. D. Iyengar and R. Kellerman, Z. Phys. Chem., N. F. 64, 1969, p. 345

"The Nature of Paramagnetic Species Observed in Ammonia-Precipitated  $\text{TiO}_2$  Powders," R. D. Iyengar and R. Kellerman, J. Catalysis 12, 1968, p. 107



## Yale University

## LOW ENERGY ELECTRON DIFFRACTION

W. D. Robertson, J. V. Florio, D. G. Fedak\*, and Robert Zimmer\*

(\* Graduate Student)

## Objective

Determination of the atomic structure and composition of surfaces.

## Approach

Surface structure, unit cell parameters and unit cell contents, are determined by low energy electron diffraction (LEED) observations. Surface composition is determined by Auger electron spectroscopy. Reactivity of surfaces and identification of reaction products are studied by flash desorption into a mass-spectrometer. All these determinations are carried out on the same surface, in the same vacuum space, as functions of pressure, temperature, and time.

## Achievements

1. To perform the operations outlined above, it is first of all necessary to develop techniques for transforming measured LEED intensity into surface structure. An optical simulation technique was first developed for this purpose (see bibliography). The results of the optical technique led to a reconsideration of the scattering mechanism, and a complete computer program for simulation. Subsequently, the entire physical process of multiple elastic and inelastic scattering of low energy electrons was formulated and is now being programmed on the Yale Computer by Dr. Brian Holland and Dr. Richard Hannum. It appears that this program, and that of C. B. Duke (at General Electric) are the only two physically realistic treatments of the LEED interpretation problem.
2. The combined operation of structure and composition analysis has been performed on silicon by Dr. John Florio with the following results, which are being submitted for publication. Auger electron emission spectroscopy has been used to identify and, with suitable calibration, to quantitatively specify chlorine surface concentrations on Si(111) surfaces. Adsorption rates of  $\text{Cl}_2$  on Si(111)7 and Si(111) $\sqrt{19}$  surfaces have been measured as a function of substrate temperature, and sticking probabilities have been subsequently calculated. The initial sticking probability is in the range 0.1 to 0.2. Adsorbed chlorine is observed to exist in two states, one, weakly bound and the other, strongly bound to the surface.

Electron beam desorption of chlorine from Si(111) surfaces can be significant with a focussed electron beam. Starting with an ordered (1x1) chlorine structure, the result of beam desorption is a disordered surface. The electron beam desorption cross-section for chlorine was calculated to be  $2 \times 10^{-19} \text{cm}^2$ .

Various LEED structures were observed for chlorine on Si(111) surfaces. These include two with chlorine monolayer concentrations, Si(111)7\*-Cl and Si(111)1\*-Cl, and a third with only a trace (4-5% of a monolayer) of chlorine present, Si(111)1. The 1x1 structures at high and low coverage are different, as shown by the voltage dependence of the reflected beam intensities.

The reaction between chlorine and the Si(111) surface follows second order kinetics in its dependence on chlorine surface concentration. The desorption reaction product is  $\text{SiCl}_4$ . From the temperature dependence of the rate constant, an activation energy of  $\sim 35 \text{ kcal/mol}$  for the desorption process was measured. A reaction mechanism, involving the surface species  $[\text{>SiCl}_2]$  which is formed on the surface ledge at the junction of (001) and (111) planes, is suggested.

Detailed analysis of the structure of silicon surfaces in different states, which can be obtained from LEED intensity data, is currently being performed. This data will also be employed to test the new formulation of the scattering problem and the computer program which calculates the intensity from an assumed structural model.

#### Publications

D. G. Fedak, T. E. Fischer, W. D. Robertson, "Surface Structure Analysis by Optical Simulation of LEED Patterns", *J. Applied Physics* **39**, 5658 (1968).

D. G. Fedak, J. V. Florio, W. D. Robertson, "The Interaction between Chlorine and the (100) Surface of Gold", to be published in *Structure and Chemistry of Solid Surfaces*, G. A. Somorjai et al., Eds., John Wiley and Sons, Inc., New York, 1969.

J. V. Florio, W. D. Robertson, "Chlorine Reactions on the Si(111) Surface", submitted to *Surface Science*, April 1969.

#### Invited Presentations

American Institute of Chemical Engineers, Annual Meeting, 1968.

Department of Materials Science, University of Pennsylvania, 1968.

International Nickel Company Research Laboratory, Sterling Forest, New York, 1968.

Kennecott Copper Corporation, Research Laboratory, Legermont, Massachusetts, 1968.

## Naval Research Laboratory

## STRESS-CORROSION CRACKING (General)

B. F. Brown

## Objective

To present general and tutorial reviews of the subject.

## Publications

"The Application of Fracture Mechanics to Stress-Corrosion Cracking," B. F. Brown, Metallurgical Reviews 13:129, Dec 1968, pp. 171-183

"Coping with the Problem of the Stress-Corrosion Cracking of Structural Alloys in Sea Water," B. F. Brown, J. Ocean Engineering 1:3, Feb 1969, pp. 291-296

"Interpreting Laboratory Stress-Corrosion Cracking Data in Materials Selection," B. F. Brown, presented at 1969 ASME Metals Engineering and Pressure Vessels & Piping Conference on Environmental Effects in Failure of Engineering Materials, Washington, D. C., 31 Mar 1969; ASME Preprint 69-MET-10

"Stress-Corrosion Cracking: A Perspective Review of the Problem," B. F. Brown, NRL Report 7130, 16 June 1970

"Corrosion Effects in Mechanical Failure; Corrosion Fatigue and Stress-Corrosion Cracking," B. F. Brown, Proc. of the 15th Meeting of the Mechanical Failures Prevention Group—MFPG Technical Report No. 8, Office of Naval Research, June 1, 1971

## Presentations

"The Application of Fracture Mechanics to Stress Corrosion and Other Cracking Problems in Advanced Metallurgical Materials," B. F. Brown, presented to the Lehigh Valley Chapter, ASM, Bethlehem, Pa., 1 Nov 1968

"The Three Facets of Stress-Corrosion Cracking," B. F. Brown, presented to Washington Section, ASM, as the 1969 Burgess Memorial Lecture, Washington, D. C., 10 Feb 1969

"Relation of Corrosion to the Use of Modern Metallurgical Alloys in the Sea," B. F. Brown, presented at Department of Ocean Engineering, Florida Atlantic University, Boca Raton, Florida, 28 Feb 1969

"Environmental Effects on Fracture," B. F. Brown, presented at Seminar in Deformation and Fracture of Engineering Materials, Carnegie-Mellon University, Pittsburgh, Pa., 17 Mar 1969

"The Fundamentals of Stress Corrosion," B. F. Brown, Lecture to graduate students in corrosion at the University of Delaware, Newark, Delaware, 29 Mar 1969

"Mechanisms of Stress-Corrosion Cracking (SCC)," B. F. Brown, presented at Rice University, Houston, Texas, 28 Apr 1969

**"Mechanisms of Stress-Corrosion Cracking (SCC)," B. F. Brown, presented at ARPA Materials Research Council Conference, Centerville, Mass., 15 July 1969**

**"Implication of Cathodic Reduction of Hydrogen to Stress-Corrosion Cracking," B. F. Brown, presented at the Symposium on Cathodic Processes and Effects of Hydrogen on Metal Properties, 136th National Meeting of The Electrochemical Society, Detroit, Michigan, 5-10 Oct 1969; to be published in Extended Abstract Book**

**"The ARPA Coupling Program on Stress-Corrosion Cracking," B. F. Brown, presented at the 1969 Tri-Service Meeting on Corrosion of Military Equipment, Annapolis, Md., 19-21 Nov 1969; to be published in Proceedings**

**"The Application of Fracture Mechanics to Stress-Corrosion Cracking," B. F. Brown, presented at the ASM Educational Conference on Fracture Control for Metal Structures, Philadelphia, Pa., 27 Jan 1970; Chicago, Ill., 21 May 1970**

**"Implications of Stress Corrosion Cracking in Materials Selection and Design," B. F. Brown, presented to the Department of Mechanical and Aerospace Engineering Seminar, University of Delaware, Newark, Delaware, 10 Apr 1970**

**"Advances in Stress Corrosion," B. F. Brown, The Institute of Materials Science Lecture Series, University of Connecticut, Storrs, Connecticut, 24 Apr 1970**

**"Stress-Corrosion Behavior of High Strength Alloy Systems," B. F. Brown, presented at the Session on Stress Corrosion, Air Force Materials Symposium '70, Miami Beach, Florida, 21 May 1970**

**"Studies on Occluded-Cell Corrosion Phenomena," B. F. Brown, The Gordon Research Conference on Corrosion, New London, N. Y., 26-31 July 1970**

**"Overview of Stress-Corrosion Cracking," B. F. Brown, presented at the ASM Educational Conference on Stress Corrosion, Philadelphia, Pa., 4 Aug 1970**

**"Stress-Corrosion Cracking," B. F. Brown, presented to Graduate Course on Behavior of Materials in the Ocean Environment, The Catholic University of America, Washington, D. C., 24-28 Aug 1970**

**"Mechanical Failures under the Combined Action of Stresses and Corrosive Environments," B. F. Brown, presented to the Meeting on Corrosion Effects in Mechanical Failure, Mechanical Failures Prevention Group, Dayton, Ohio, 14-15 Apr 1971**

## Naval Research Laboratory

**STRESS-CORROSION CRACKING IN TITANIUM (General)****E. P. Dahlberg and B. F. Brown****Objectives**

To present or publish, or both, general reviews on stress-corrosion cracking in titanium alloys.

**Publications**

"An Annotated Bibliography of Recent Papers and Reports on the Subject of Ambient Temperature Aqueous Stress-Corrosion Cracking of Titanium and Titanium Alloys,"  
E. P. Dahlberg, NRL Bibliography Report 29, Oct. 1966

**Presentations**

"Theory and Technology of Stress-Corrosion Cracking in Titanium Alloys,"  
B. F. Brown, presented at Bureau of Mines, College Park, Maryland, 30 Apr 1969

"Titanium Alloys in the Marine Environment," B. F. Brown, presented at the Symposium on Titanium for the Chemical Engineer, National Meeting of the American Institute of Chemical Engineers, Atlanta, Georgia, 15-18 Feb 1970; Monograph on Symposium on Titanium for the Chemical Engineer, in press

## Naval Research Laboratory

## CORROSION FATIGUE PROCESSES IN ALUMINUM ALLOY

D. A. Meyn

## Objective

To examine the difference between the propagation of cracks in an inert environment and in (humid) air.

## Approach

Crack propagation experiments were conducted on aluminum alloy in vacuum and in (humid) air using fracture mechanics to quantify the stress factor. The fracture surfaces were studied by replication electron fractography.

## Publication

"The Nature of Fatigue-Crack Propagation in Air and Vacuum for 2024 Aluminum,"  
D. A. Meyn, ASM Trans. 61:1, Mar 1968, pp. 52-61

## Naval Research Laboratory

**DIAGNOSTIC CRITERION FOR STRESS-CORROSION  
CRACKING IN ALUMINUM ALLOYS**

D. A. Meyn and J. E. Flint

**Objective**

To examine corrosion product films on Al-Zn-Mg stress-corrosion cracking specimens for indications to differentiate SCC from other fracture modes.

**Achievements**

The pattern of fractured corrosion product films known as "mud-crack pattern" is a reliable method for positive identification of SCC when it is seen, but it may be missing over a large portion of the SCC surface.

**Publications**

"Fractographic Diagnosis of Stress-Corrosion Cracking in Al-Zn-Mg," D. A. Meyn, *Corrosion* 26:10, Oct 1970, pp. 427-429

## Naval Research Laboratory

## ELECTROCHEMISTRY OF STRESS-CORROSION CRACK TIPS

B. F. Brown, E. P. Dahlberg, C. T. Fujii, M. H. Peterson, and J. A. Smith

## Objective

To determine and analyze the electrochemical conditions within growing stress-corrosion cracks.

## Approach

Three approaches have been tried in order to determine the thermodynamic conditions (pH and E) corresponding to either stress-corrosion cracking initiation or growth:

- 1) Potentiostating smooth stressed specimens in buffered solutions of known pH,
- 2) freezing (liquid N) specimens with growing cracks, opening crack wide, and analyzing corroder as it thaws, and 3) theifing corroder at intersection of crack with edge of specimen and making instantaneous determination of pH at crack front using antimony electrode or glass electrode.

## Achievements

The pH at a growing crack tip in all alloy steels is about 4, as determined by pH papers, antimony electrode, and glass electrode. The acid condition is due to hydrolysis. Potentiostating to various potentials causes large changes in cracking kinetics, but regardless of alloy content, the minimum in kinetics is at about -0.85 or -0.9 volts SCE. This potential corresponds to that for the thermodynamic stability for iron in water. Regardless of alloy or potential, while cracking is occurring the conditions at the crack tip are favorable for the reduction of hydrogen, and only the hydrogen mechanism is required to explain SCC in high strength steels. There is no basic reason why a given area (e.g., the crack tip) cannot be simultaneously an anode for iron dissolution and a cathode for hydrogen reduction.

The pH at the tips of growing cracks in aluminum alloys is about 3.2-3.5, and in titanium alloys about 1.6. Cathodic polarization tends to neutralize this acidity and thereby to reduce cracking kinetics. The addition of  $\text{CuCl}_2$  decreases cracking kinetics in titanium alloys, probably by substituting the reduction of copper for the reduction of hydrogen.

## Publications

"A Technique for Measuring the pH of Aqueous Solutions Within a Propagating Stress-Corrosion Crack," E. P. Dahlberg, C. T. Fujii, and B. F. Brown, Rept/NRL Prog., Aug. 1968, pp. 28-29

"Methods for Studying the Solution Chemistry Within Stress Corrosion Cracks," B. F. Brown, C. T. Fujii, and E. P. Dahlberg, J. Electrochem Soc. 116:2, Feb 1969, pp. 218-219

"On the Electrochemistry of Stress-Corrosion Cracking of High Strength Steels," B. F. Brown, Bulletin of CEBELCOR 8, March 1969, pp. E. 76/1-4



"Solution Chemistry Within Stress-Corrosion Cracks in Alloy Steels," G. Sandoz, C. T. Fujii, and B. F. Brown, *Corrosion Science* 10:12, Dec 1970, pp. 839-845

"A Method for the Direct Measurement of the Electrochemical Conditions at an Advancing Crack Front," J. A. Smith and M. H. Peterson, *Rept/NRL Prog.*, Jan 1970, pp. 32-33

"On the Existence of a Threshold Stress for Corrosion Cracking in Titanium Alloys in Salt Water," B. F. Brown, *Journal of Materials* 5:4, Dec 1970, pp. 786-791

"Mechanism(s) of Stress Corrosion of High Strength Steels as Deduced Using Indicator Papers," B. F. Brown, *Acta Mexicana de Ciencia y Tecnologia*, in press

"Electrochemical Conditions at the Tip of an Advancing Stress Corrosion Crack in AISI 4340 Steel," J. A. Smith, M. H. Peterson, and B. F. Brown, *Corrosion* 26:12, Dec 1970, pp. 539-542

#### Invited Talks

"Thermodynamic Conditions at the Tips of Growing Stress-Corrosion Cracks in High Strength Steels," B. F. Brown, presented at the Belgian-American Symposium, CEBELCOR, Brussels, Belgium, 3-4 Sept 1969

"Solution Chemistry Within Stress-Corrosion Cracks in Titanium Alloys," B. F. Brown, presented at the ASM Materials Engineering Congress, Philadelphia, Pa., 15 Oct 1969

"Advances in Stress Corrosion," B. F. Brown, presented at the University of Connecticut, Storrs, Connecticut, 24 Apr 1970

"Solution Chemistry Within Stress-Corrosion Cracks in Titanium 8-1-1 Alloy," B. F. Brown, presented to the International Symposium on Stress Corrosion Mechanisms in Titanium Alloys, Atlanta, Georgia, 27-29 Jan 1971

## Naval Research Laboratory

## STEELS

G. Sandoz, M. H. Peterson, J. A. Smith, B. F. Brown, and E. P. Dahlberg

## Objective

To determine the resistance of high strength steel to stress-corrosion cracking and to further extend our knowledge of the mechanisms involved.

## Approach

Determine the threshold values of stress intensity for stress corrosion cracking in salt water for high strength steels. Study the chemistry of reactions within propagating cracks. Study the effect of individual alloying elements.

## Achievements

The susceptibility to stress-corrosion cracking in salt water of a number of high strength steels at various levels of yield strength was measured. The susceptibility of the steels increases with increasing yield strength. Among commercial steels, the higher alloy steels are generally superior, but there are wide variations within any one steel class because of sensitivity to processing variables. In quenched-and-tempered steels the elements C and Mn lower markedly the threshold stress intensity parameter for stress-corrosion cracking; the elements Cr, Ni, Co, Mo, S, and P have little effect.

It was shown that the solution within propagating stress-corrosion cracks in a wide variety of high strength steels has a pH of 3.6-3.8. The metallic elements are in the solution in about the same proportions as in the alloy. A mechanism involving embrittlement from hydrogen released by corrosion reaction explains the observations.

## Publications

"Stress-Corrosion Cracking Resistance of an 18Ni 200 Grade Maraging Steel Base Plate and Weld," G. Sandoz and R. L. Newbegin, NRL Memorandum Report 1772, Mar 1967

"Analysis of Environmental Cracking in 4340 Steel by Scanning Electron Microscopy," E. P. Dahlberg and E. J. Brooks, Rept/NRL Prog, Jan 1969, pp. 23-24

"The Effect of Carbon Content on the Stress-Corrosion Cracking Susceptibility of Quenched-and-Tempered Low Alloy Steels," G. Sandoz, R. L. Newbegin, and B. F. Brown, Rept/NRL Prog, July 1969, pp. 28-29

"Effect of Some Elements on the Susceptibility to Stress-Corrosion Cracking," G. Sandoz, Navy Materials Bulletin III:3, Navy Advisory Council on Materials, Oct 1969, p. 7

"The Effect of Manganese Content on the Stress-Corrosion Cracking Susceptibility of Quenched-and-Tempered Fe-C-Mn Alloys in Salt Water," G. Sandoz and R. L. Newbegin, Rept/NRL Prog, Feb 1970, pp. 26-29

"The Effects of Sulfur Content on the Stress-Corrosion Cracking Susceptibility of Quenched-and-Tempered Steel Similar to AISI 4340," G. Sandoz and R. L. Newbegin, Rept/NRL Prog, May 1970

"Electrochemical Conditions at the Tip of an Advancing Stress-Corrosion Crack in AISI 4340 Steel," J. A. Smith, M. H. Peterson, and B. F. Brown, Corrosion 26:12, Dec 1970, pp. 539-542

"Solution Chemistry Within Stress-Corrosion Cracks in Alloy Steels," G. Sandoz, C. T. Fujii, and B. F. Brown, Corrosion Science 10:12, Dec 1970, pp. 839-845

"The Effects of Alloying Elements on the Susceptibility to Stress-Corrosion Cracking of Martensitic Steels in Salt Water," G. Sandoz, Metallurgical Transactions 2:4, Apr 1971, pp. 1055-1063

"Mechanism(s) of Stress Corrosion of High Strength Steels As Deduced Using Indicator Papers," B. F. Brown, Acta Mexicana de Ciencia y Tecnologia, in press

"Stress-Corrosion Cracking of High Strength Steels," B. F. Brown, Proceedings of the NATO Conference on the Theory of Stress Corrosion Cracking in Alloys, in press

"The Resistance of Some High Strength Steels to Slow Crack Growth in Salt Water," G. Sandoz, submitted to Journal of Materials

#### **Presentations**

"The Susceptibility to Slow Crack Growth of Some High Strength Steels in Salt Water," G. Sandoz, presented to the ASTM Fall Meeting, Atlanta, Georgia, 2 Oct 1968

"Fractographic Analysis of Stress-Corrosion Cracking in High Strength 4340 Steel," E. Philip Dahlberg, presented at 1969 WESTEC Conference, Los Angeles, California, 13 Mar 1969

"The 'Hydrogen-or-Nothing' Model for Environmental Cracking of Alloy Steels," B. F. Brown, presented at Naval Air Development Center, Philadelphia, Pa., 6 May 1969

"Implication of Cathodic Reduction of Hydrogen to Stress-Corrosion Cracking," B. F. Brown, presented at the Symposium on Cathodic Processes and Effects of Hydrogen on Metal Properties, 136th National Meeting of The Electrochemical Society, Detroit, Michigan, 5-10 Oct 1969

"Stress-Corrosion Cracking of High Strength Steels," G. Sandoz, presented at the 1970 Westec Conference, Session on Stress Corrosion, Los Angeles, California, 9-12 Mar 1970

"Mechanism(2) of Stress Corrosion of High Strength Steels As Deduced Using Indicator Papers," presented at the Latin American Colloquium on Corrosion and Protection of Materials, Mexico City, 8-10 June 1970

"Stress-Corrosion Cracking of High Strength Steels, B. F. Brown, presented at the NATO Conference on the Theory of Stress Corrosion Cracking in Alloys, Ericeira, Portugal, 29 Mar 1971

## Naval Research Laboratory

DEVELOPMENT OF STRESS-CORROSION CRACKING SPECIMENS  
AND TEST METHODS

E. P. Dahlberg, C. D. Beachem, J. E. Flint, G. Sandoz, and R. L. Newbegin

## Objective

To develop specialized specimens for determining stress-corrosion cracking (SCC) characteristics for both research and technology.

## Approach

Specimens were sought which would contain a precrack and would be analyzable by fracture mechanics methods.

## Achievements

A small specimen suitable for SCC tests of sheet material was designed and compliance measurements were made. When the notched specimen is stressed by a wedge to a measured displacement and is then exposed to a corrodent, a stress-corrosion crack propagates until the crack tip has reached a region where the stress is too low to propagate the crack further. This condition is defined as  $K_{I_{SCC}}$  for arrest, and the K number can be determined from the compliance calibration, the crack length, and the displacement. The specimen is thus similar to the Manjoine specimen which had been adopted by Rolfe for SCC testing, except that the present specimen is suitable for sheet material. An equivalent specimen was designed for thick plate and was stressed by an elastic ring which relaxed as the crack grew, again permitting a crack-arrest characterization. A simple constant K specimen has been demonstrated useful for SCC kinetic studies; this specimen, designated the double torsion specimen, can be made from sheet material with a minimum of machine work.

## Presentations

None.

## Publications

"Stress-Corrosion-Cracking Test Methods," E. P. Dahlberg, Rept/NRL Prog, Oct 1967, pp. 41-42

"Stress-Corrosion-Cracking Characteristics of Several Aluminum Alloys by a Crack-Arrest Method," E. P. Dahlberg, Rept/NRL Prog, Jan 1968, pp. 23-24

"A Self-Stressed Specimen for Measuring Stress-Corrosion Cracking in Aluminum Alloys," E. P. Dahlberg, Rept/NRL Prog, April 1968, pp. 25-27

"Characterizing Stress-Corrosion Cracking in a 7079-T651 Aluminum Alloy by Using a Self-Stressed Double Cantilever Beam Specimen," E. P. Dahlberg, Rept/NRL Prog, Aug 1968, pp. 25-28

"Compliance Measurements for a Simple (WOL) Stress-Corrosion Cracking Test Specimen," E. P. Dahlberg and J. E. Flint, Rept/NRL Prog, Oct 1968, pp. 20-21

"A Constant K Specimen for Stress Corrosion Cracking Testing," C. D. Beachem, J. A. Kies, and B. F. Brown, Materials Research & Standards 11:4, April 1971, p. 30

## Naval Research Laboratory

## SCC IN TITANIUM

G. Sandoz, E. P. Dahlberg, R. L. Newbegin, and D. A. Meyn

## Objective

To determine the effects of various environments on titanium alloys and use this information to determine the mechanisms of stress-corrosion cracking.

## Approach

Use the cantilever beam test or the wedge load-type specimen test, or both, to determine values of  $K_{I_{SCC}}$ .

## Achievements

Found that dissolved hydrogen in titanium alloys produces effects similar to effects of some environments. Generally, a common fracture plane is favored, regardless of the environment. Environment may be organic and need not be an electrolyte to produce cracking. Values of threshold stress intensity are similar in all organic environments, but values in water and methanol are somewhat lower.

## Publications

"Effects of Some Organics on the Stress Corrosion Susceptibility of Some Titanium Alloys," G. Sandoz, DMIC Memorandum 228, Battelle Memorial Institute, 6 Mar 1967, pp. 10-15

"Stress Corrosion Cracking Susceptibility of a Titanium Alloy in a Non-electrolyte," G. Sandoz, *Nature* 214, 8 April 1967, pp. 166-167

"Fractography and Crystallography of Subcritical Crack Propagation in High Strength Titanium Alloys," D. A. Meyn and G. Sandoz, *Trans. TMS/AIME* 245, June 1969, pp. 1253-1258

"Subcritical Crack Propagation in Ti-8Al-1Mo-1V Alloy in Organic Environments, Salt Water, and Inert Environments," G. Sandoz, *Proceedings of Conference on Fundamental Aspects of Stress Corrosion Cracking*, NACE, Houston (1969), pp. 684-690

"Thin Foil Electron Microscopy," E. P. Dahlberg, *Rept/NRL Prog*, Apr 1967, pp. 19-21

"Delayed Fracture Characteristics of Ti-8Al-1Mo-1V Alloy," G. Sandoz, *Rept/NRL Prog*, May 1967, pp. 31-32

"Effect of Specimen Breadth on Susceptibility to Stress-Corrosion Cracking of Ti-8Al-1Mo-1V Alloy in Salt Water," G. Sandoz and R. L. Newbegin, *Rept/NRL Prog*, Aug 1967, pp. 45-46

"Delayed Failure of Ti-7Al-2Cb-1Ta Under Mode III Loading in Air, Salt Water and Methanol," D. A. Meyn, *Rept/NRL Prog*, Nov 1967, pp. 33-34

**"Effect of Hydrogen Content on Subcritical Crack Growth in Ti-8Al-1Mo-1V Alloy,"**  
G. Sandoz and R. L. Newbegin, Rept/NRL Prog, Nov 1967, pp. 35-36

**"Stress-Corrosion Cracking Tests of Surface Flawed Specimens of Ti-7Al-2Cb-1Ta,"**  
R. W. Judy, Jr., and E. P. Dahlberg, Rept/NRL Prog, May 1968, pp. 30-31

**"Effects of Hydrogen Content and Environment on Subcritical Crack Growth in Ti-7Al-2Cb-1Ta and Ti-6Al-4V Alloys,"** G. Sandoz and R. L. Newbegin, Rept/NRL Prog, Nov 1968, pp. 31-32

**"Subcritical Cracking of Ti-8Al-1Mo-1V in Mercury,"** D. A. Meyn and E. P. Dahlberg, Rept/NRL Prog, Mar 1969, pp. 17-18

#### **Presentations**

**"Evaluation of Some Stress-Corrosion Cracking Characteristics of Aluminum Alloys Using Precracked Specimens,"** E. P. Dahlberg, presented to the ASTM Fall Meeting, Atlanta, Georgia, 3 Oct 1968

**"Solution Chemistry Within Stress-Corrosion Cracks in Titanium 8-1-1 Alloy,"** B. F. Brown, presented to the International Symposium on Stress Corrosion Mechanisms in Titanium Alloys, Atlanta, Georgia, 27-29 Jan 1971

## Naval Research Laboratory

## TOPOLOGY OF STRESS-CORROSION CRACKING FRACTURES IN TITANIUM

D. A. Meyn

## Objective

To examine the details of stress-corrosion cracks in titanium alloys.

## Approach

Replica electron fractography was used on laboratory specimens and on a specimen from an Apollo fuel cell tankage failure analysis.

## Achievements

The fracture of Ti-6Al-4V by SCC in methanol demonstrated that the relative proportion of cleavage, peculiar to SCC in Titanium alloys, and mechanical rupture (by microvoid coalescence) depends upon stress intensity  $K$ . When  $K$  is low, most of the fracture is by cleavage; when  $K$  is high, there is a high proportion of microvoid coalescence, and thus the total process is a mixture of two mechanisms.

## Publications

"Effect of Crack Tip Stress Intensity on the Mechanism of Stress-Corrosion Cracking of Titanium-6Al-4V in Methanol," D. A. Meyn, Corrosion Science 7:10, Oct 1967, pp. 721-723



## Naval Research Laboratory

## THE CONCEPT OF THE OCCLUDED CORROSION CELL

B. F. Brown

## Objective

To analyze the process of stress-corrosion cracking (SCC) and the other forms of localized corrosion, such as pitting, crevice corrosion, intergranular corrosion, filiform corrosion, and exfoliation.

## Achievements

It is concluded that the corrodent within all these local corrosion cells is acid by reason of hydrolysis and that it remains acid because of the restricted communication with the outside environment. This acidity militates against repassivation. Cathodic protection is effective in both preventing and stopping this form of attack by increasing the pH to the level at which protective metal oxides or hydroxides will form. (In alloys susceptible to hydrogen cracking, cathodic protection against SCC may not be a satisfactory solution.) This work has led to the organization (largely by Dr. Roger Staehle of Ohio State University) of an International Conference on the Occluded Corrosion Cell to be held in December 1971.

## Publications

"The Role of the Occluded Corrosion Cell in Stress-Corrosion Cracking of High Strength Steels," B. F. Brown, CEBELCOR's Rapports Techniques 112, Jan 1970, pp. RT 170/1-3

"The Concept of the Occluded Corrosion Cell," B. F. Brown, Corrosion 26:8, Aug 1970, pp. 249-250

## Presentations

"New Light on the Solution Chemistry of Stress-Corrosion Cracking," B. F. Brown, presented as the RESA Lecture at the Naval Research Laboratory, Washington, D. C., 19 Nov 1968, consequent to the receipt of the E. O. Hulburt Award

"Three Forms of Occluded-Cell Corrosion," B. F. Brown, presented at National Bureau of Standards, Gaithersburg, Maryland, 14 Apr 1969

"Studies on Occluded-Cell Corrosion Phenomena," B. F. Brown, presented at the Gordon Research Conference on Corrosion, New London, N. Y., 26-31 July 1970

## Naval Research Laboratory

APPLICATION OF TENSILE LIGAMENT INSTABILITY MODEL  
TO STRESS-CORROSION PROBLEMS

J. M. Krafft and A. M. Sullivan

## Objective

To apply the ligament instability model to studies of stress-corrosion in an attempt to provide a consistent explanation of observed time to fracture and crack growth rate data.

## Approach

A model which attributes stress-corrosion crack growth rate to erosive surface attack of  $d_T$  size ligaments is proposed. The ratio of surface reaction rate  $V_s$  and crack growth rate  $V_c$  can readily be evaluated from details of the stress strain curve. Relative specimen life  $t_f$  can be estimated from the summation. The model is examined by comparing the life time, or crack velocities, of notched bend specimens in aggressive environments with bulk plastic flow properties.

## Achievements

Using either time to fracture or crack velocity data, generated as functions of the stress intensity factor  $K_I$ , substantial agreement with the material property dependent  $V_c/V_s$  curve is evident. Thus, the validity of this essentially mechanical model is demonstrated. Indicating the essential  $V_c$  curve shape it provides a rationale both for the threshold and observed non-sensitivity of velocity to  $K_I$  level.

Estimates of surface reaction rates,  $V_s$ , are also possible which agree well with the few published values.

Further calculations combining ligament area and  $V_s$  can generate information concerning the weight of metal involved in the corrosion process, which has been confirmed by micro-chemical analysis.

## Publications

"Role of Local Dissolution in Corrosion-Assisted Cracking of Titanium Alloys," J. M. Krafft, Rept/NRL Prog, March 1967, pp. 6-18

"Dissolution Velocities of Different Organic Media," A. M. Sullivan, Rept/NRL Prog, April 1967, pp. 18-19

"Tensile-Ligament Instability and the Growth of Cracks in High Strength Alloys," J. M. Krafft and J. H. Mulherin (Frankford Arsenal), Trans ASM, 62, 1 March 1969, pp. 64-81

"Weight of Metal Involved During Progress of a Stress Corrosion Crack," A. M. Sullivan, Rept/NRL Prog, March 1969, pp. 18-19

**"Velocity of Stress-Corrosion Cracks," A. M. Sullivan, Rept/NRL Prog, July 1969, pp. 30-31**

**"Velocity of Cracks Extending Under Stress in an Adverse Environment," A. M. Sullivan, Proceedings of Second International Conference on Fracture, Brighton, England, April 1969**

#### **Presentations**

**"Environmental Effects on Crack Growth Rates with Sustained and Repeated Load Cycles," J. M. Krafft and A. M. Sullivan, Invited talk at Symposium on Practical Aspects of Fatigue and Fracture, Derby, England, March 1970**

**"Stress-Corrosion Crack Velocity in 4340 Steel," A. M. Sullivan, presented to the 4th National Symposium on Fracture Mechanics, Pittsburgh, Pennsylvania, Aug 1970; to be published in Journal of Engineering Fracture Mechanics**

## Naval Research Laboratory

## DUAL SCC-RATIO ANALYSIS DIAGRAMS FOR HIGH STRENGTH STRUCTURAL MATERIALS

R. W. Judy, Jr., and R. J. Goode

## Objective

The objective of the dual SCC-RAD approach was to provide interpretative procedures for relating laboratory  $K_{Isc}$  data to materials applications.

## Approach

Fracture mechanics technology provides equations to relate  $K_{Ic}$  values determined in the laboratory to flaw size-stress level relationships for fracture. Ratio Analysis Diagram (RAD) procedures have been evolved to make engineering assessments of conditions for fast fracture of the entire strength range of high strength metals. Expression of stress-corrosion cracking (SCC) characteristics in fracture mechanics parameters permits the effects of hostile environments on the same structural metals to be included in the RAD framework.

## Achievements

Dual SCC-RAD procedures were derived for high strength steels and for titanium alloys. The ASTM E24 Committee's recommendations for specimen dimensions in  $K_{Ic}$  testing were imposed for the SCC specimens to determine a thickness requirement. The thickness requirement was necessary to separate plane strain and plane stress fracture conditions. With these criteria, SCC data were added to the RAD for steels and the RAD for titanium alloys by using the existing  $K_{Ic}$  scales. The thickness criteria were included on the RADs in the form of lines of constant ratio  $K_{Isc}/\sigma_{ys}$ ; the value of the ratio depended on the thickness of the specimen involved. A region of SCC tunnelling was defined for which  $K_{Isc}$  values cannot be obtained. Below this region  $K_{Isc}$  measurements are possible, and engineering interpretation of flaw size-stress level conditions for SCC and for fast fracture can be made.

## Publications

"Stress-Corrosion Cracking Characterization Procedures and Interpretations to Failure-Safe Use of Titanium Alloys," R. W. Judy, Jr. and R. J. Goode, NRL Report 6879, 8 April 1969; ASME Journal of Basic Engineering 91, Series D(4), Dec. 1969, pp. 614-617

"Procedures for Stress-Corrosion Cracking Characterization and Interpretation to Failure-Safe Design for High Strength Steels," R. W. Judy, Jr. and R. J. Goode, NRL Report 6988, 29 Nov. 1969

## Naval Research Laboratory

**EFFECTS OF HEAT-TREATMENT ENVIRONMENTS ON THE STRESS-CORROSION CRACKING RESISTANCE OF TITANIUM ALLOYS**

D. G. Howe and R. J. Goode

**Objective**

The objective was to determine the effects of heat-treatment environments on the salt water stress-corrosion cracking (SCC) characteristics of four titanium alloys.

**Approach**

Cantilever bend tests were conducted in 3 1/2% salt water environments for samples of Ti-8Al-1Mo-1V, Ti-7Al-1Mo-1V, Ti-6Al-4V, and Ti-7Al-2.5Mo alloys which had been heat treated and aged in helium or argon atmospheres or in vacuum. The  $K_{Isc}$  data for the various environments were compared.

**Achievements**

The  $K_{Isc}$  characteristics were determined for a variety of heat-treating conditions involving different furnace environments at each step. Vacuum solution annealing and cooling in a helium atmosphere resulted in material immune to salt water SCC for all four alloys. Heat treatments in argon or helium atmospheres resulted in  $K_{Isc}$  values that were dependent on the solution annealing temperature rather than the heat treating environment. The results of chemical analyses of the interstitial hydrogen content of all materials tested indicated a conjunctive relationship between the salt water SCC resistance and the interstitial hydrogen content of the material.

**Publications**

"Effects of Heat Treating Environmental Conditions on the Stress-Corrosion Cracking Resistance of Several Titanium Alloys," D. G. Howe and R. J. Goode, ASTM STP 432, (1968) pp. 189-201

"Effects of Heat Treatment Environmental Conditions on Stress-Corrosion Cracking Resistance of Several Titanium Alloys," D. A. Howe, Rept/NRL Prog, Feb 1967, pp. 32-35

"Effects of Heat-Treatment on the Stress-Corrosion-Cracking Resistance of the Alloy Ti-6Al-6V-2.5Sn," D. G. Howe, Rept/NRL Prog, Sept 1967, pp. 51-52

## Naval Research Laboratory

## CHARACTERISTICS OF STRESS-CORROSION CRACKING RESISTANCE OF HIGH STRENGTH TITANIUM ALLOYS

R. W. Judy, Jr., R. J. Goode, and R. W. Huber

## Objective

The objective of these studies was the determination of the effects of salt water (simulated seawater) environments on structural titanium alloys.

## Approach

Cantilever bend tests were conducted for a wide variety of titanium alloys in a 3 1/2 wt-% salt water environment. The SCC threshold ( $K_{I_{SCC}}$ ) values were compared with mechanical property data.

## Achievements

Characteristic  $K_{I_{SCC}}$  values were determined for a wide variety of titanium alloy plate materials and metal-inert-gas (MIG) and electron-beam (EB) weldments. These represented one-inch-thick materials with variations of heat-treated conditions and welding parameters. It was shown that comparison of salt water SCC resistance of titanium alloys was not related to other mechanical properties of the material. Interpretation of the  $K_{I_{SCC}}$  data to predictions of critical flaw size for yield stress loading was summarized on a SCC-index diagram based on linear elastic fracture mechanics.

## Publications

"Stress-Corrosion Cracking Characteristics of Alloys of Titanium in Salt Water," R. W. Judy, Jr., and R. J. Goode, NRL Report 6564, 21 July 1967

"Fracture Toughness and Stress-Corrosion Cracking of Some Titanium Alloy Weldments," R. W. Huber, R. J. Goode, and R. W. Judy, Jr., Welding Journal Research Supplement 32: 10, October 1967, pp. 1-9

"Fractographic Study of Titanium Alloy SEN Fracture Mechanics Specimens," R. W. Judy, Jr., and R. J. Goode, Rept/NRL Prog, Nov 1966, pp. 18-20

"Stress-Corrosion-Cracking Characterization Studies of High Strength Titanium Alloy Weldments," R. W. Judy, Jr., A. Friedland, and R. J. Goode, Rept/NRL Prog, Nov 1966, pp. 20-21

"Stress-Corrosion-Cracking Characteristics of Alloys of Titanium in Salt Water," R. W. Judy, Jr., and R. J. Goode, NRL Report 6564, 21 July 1967

"Stress-Corrosion-Cracking Behavior in Titanium Alloys," R. W. Judy, Jr., and R. J. Goode, Rept/NRL Prog, July 1967, pp. 38-40

"Fracture Toughness and Salt-Water Stress-Corrosion-Cracking Resistance of Titanium Alloy Weldments," R. W. Huber, R. J. Goode, and R. W. Judy, Jr., Rept/NRL Prog, Nov 1967, pp. 1-11

**"Study of Notch Acuity on the SCC Characteristics of Titanium Alloys,"  
R. W. Judy, Jr., and R. J. Goode, Rept/NRL Prog, Nov 1967, pp. 34-35**

**"Procedures for Stress-Corrosion Cracking Characterization and Interpretation  
to Failure-Safe Design for High Strength Steels," R. W. Judy, Jr., and R. J.  
Goode, NRL Report 6988, 29 Nov 1969**

## Naval Research Laboratory

## IRON HYDRIDE PREPARATION

Forrest L. Carter and M. O'Hara

## Objective

To prepare and characterize the iron hydrides which are logical precursors to the understanding of the role hydrogen plays in the stress-corrosion cracking of steels.

## Approach

The preparation of the iron hydrides is being attempted by four different chemical methods involving glove box procedures to provide an inert working atmosphere. These are: 1) The Grignard reaction between phenylmagnesium bromide and an anhydrous iron chloride in the presence of purified hydrogen, 2) the reaction between pyrophoric aluminum triethyl and an iron chloride in the presence of hydrogen, 3) the electrolysis of ammonium chloride in liquid ammonia using iron electrodes, and 4) the sputtering of iron via argon-hydrogen bombardment. In this latter method it is hoped that the atomic iron produced by energetic argon ions will react with hydrogen while it is in the finely divided state.

## Achievements

It has been shown that the earlier work using the Grignard-reaction (1, above) is in error in that one obtains not the transition metal hydrides, but rather transition metal ether complexes of low hydrogen content (as hydride). Using the second method involving triethyl aluminum, small quantities of a black crystalline paramagnetic powder have been obtained. This material, containing iron, hydrogen, and 10-20% aluminum, is readily indexed as BCC with a  $3.30\text{\AA}$  cell edge compared with BCC iron, the unit cell volume is 50% greater, and generally appears to be related to the iron hydride sought. It is possible that the compound is stabilized by the incorporation of aluminum, for which well-characterized hydrides are known. An alternate synthesis of this "iron aluminum hydride" is being attempted via the reaction of iron trichloride with the alkali aluminum hydrides. A reaction intermediate involving tetrahydrofuran has been obtained using  $\text{LiAlH}_4$ . The decomposition of this product will be attempted by refluxing in a hydrocarbon solvent. The electrolysis of ammonium chloride in liquid ammonia gave no detectable change in the x-ray powder pattern of an iron wire electrode. However, the electrolysis of a liquid ammonia-ammonium chloride electrolyte containing  $\text{FeCl}_3$  did yield a brown deposition on a platinum wire cathode. Difficulties in the isolation of this deposit have prevented its characterization to date. Definitive results for the argon bombardment method are yet to be obtained.



## Naval Research Laboratory

## POTENTIOSTATIC BEHAVIOR AND PASSIVATION OF ANODIC REACTIONS OF IRON AND PLATINUM

S. Schuldiner

## Objective

The electrochemical behavior of iron and platinum has been investigated in closed high purity systems. Especial attention was paid to determination of the mechanism of passivation.

## Approach

Steady-state potentiostatic polarization curves were determined under conditions in which reactable impurities were reduced by pre-electrolysis to extremely low levels. Effects of added impurities were determined after the behavior under high purity conditions was determined. Effects of anion adsorption were determined under both steady-state and transient conditions.

## Achievements

Over a dozen identifying characteristics due to small amounts of impurities were described and most of the interfering impurities were reduced to a level of less than one part in  $10^{12}$ . Under these conditions, iron gave results similar to platinum and acted as a noble metal, showing no corrosion at any applied potential. Current densities were only a few percent of those given in the literature where iron corroded under conditions of ordinary purity. The high purity system can act as a standard for determining electrode reactions and the nature of passivation and was used here to evaluate quantitatively the effect of adding various amounts of chloride ion to the system, thus showing the initiation of corrosion and of passivity. A mechanism of inert anion adsorption on the passive behavior of the hydrogen oxidation reaction on platinum was demonstrated under both steady-state and transient conditions.

## Publications

"Passivation of Anodic Reactions," S. Schuldiner, Rept/NRL Prog, March 1968, p. 21; J. Electrochem. Soc. 115, Sept 1968, p. 897; and NRL Report 6703, 30 Apr 1968

"Anodic Oxidation of Hydrogen on Iron and Platinum in Sodium Hydroxide Solution," S. Schuldiner and C. M. Shepherd, J. Electrochem. Soc. 115, Sept 1968 p. 916; and NRL Report 6718, 24 May 1968

"Potentiostatic Current-Potential Measurements on Iron and Platinum Electrodes in High-Purity Closed Alkaline Systems," C. M. Shepherd and S. Schuldiner, J. Electrochem. Soc. 115, 1968, p. 1124; and NRL Report 6748, 26 Aug 1968

"Effect of Chloride Ion on Corrosion of Iron," C. M. Shepherd and S. Schuldiner, submitted to Corrosion Science

**"Characterization of Platinum Electrodes in Sulfuric Acid Solution. I. Transient Conditions,"** M. Rosen, D. R. Flinn, and S. Schuldiner, submitted to the Journal of the Electrochemical Society

#### **Presentations**

Each of the above papers has been given at technical meetings. In addition, the following have been presented:

**"Passive Films,"** S. Schuldiner, presented at the ARPA-IDL Navy Briefing, NSRDC (David Taylor Model Basin), Nov 2, 1967

**"Passivation of Platinum and Iron in High-Purity Systems,"** S. Schuldiner, presented at the Gordon Research Conference on Corrosion, July 24, 1968

**"Mechanisms of Passivation of Anodic Reactions on Inert Electrodes,"** S. Schuldiner, presented at the University of Pennsylvania, Chemistry Seminar, Philadelphia, Pa., Nov 6, 1968

## Naval Research Laboratory

## ROLE OF CHLORIDE IONS IN STRESS-CORROSION CRACKING

T. A. Kovacina and D. L. Venezky

## Objective

Determine distribution of chloride ion between liquid (sodium chloride solution) and solid [iron (IV) oxide] phases and determine the reaction mechanisms involved.

## Approach

Specific ion electrodes ( $H^+$  and  $Cl^-$ ) and the radioisotope  $^{36}Cl_{17}$  are used to monitor the effect of the addition of  $\alpha Fe_2O_3$  to various aqueous solutions.

## Achievements

Additions of pure  $\alpha Fe_2O_3$  (<10 ppm total impurities) to carbon dioxide free water or aqueous sodium chloride solutions resulted in significant changes in the hydrogen ion concentrations of the solutions. The results are consistent with a postulated initial hydration of the solid oxide surface, followed by acidic or basic hydrolysis, depending on the environment. Although a much weaker base than the hydroxide ion, the chloride ion appears to successfully replace hydroxide ions on the hydrated oxide surface.

## Publication

"Investigations of Selective Interactions of the Iron/Aqueous Sodium Chloride System. Part 1—The Adsorption of Chloride Ion by  $\alpha$ -Iron (III) Oxide in Oxygen-Saturated Sodium Chloride Solutions at 30°C," T. Kovacina and D. L. Venezky, NRL Report 7264, May 1971

## Naval Research Laboratory

**EFFECT OF CHEMICAL ENVIRONMENT ON STRESS-CORROSION  
CRACKING OF METALS**

H. R. Baker and C. R. Singleterry

**Objective**

To define chemical factors influencing stress-corrosion cracking (SCC) of metals and to identify chemical inhibitors of SCC.

**Approach**

SCC of U-bend specimens is studied under conditions of controlled pH, temperature, and ionic environment. The effect of corrosion inhibitors on SCC is examined as a function of these variables.

**Achievements**

Conditions have been established for the rapid SCC of 4340 steel in various salt solutions. It has been shown that conventional inhibitors of steel corrosion are effective in preventing SCC of this alloy, but that the inhibitors must be present at much higher concentrations than are required for the prevention of surface corrosion. As could be expected from the observations of the characteristic pH encountered in stress-corrosion cracks, the presence of an adequate alkaline reserve, by itself or in conjunction with conventional inhibitors, exerted a marked inhibiting effect. A report of this work is in preparation. Suitable buffering of chromate solutions has also been shown to delay the SCC of 7075 T aluminum alloy. Corrosion of 4340 alloy in boiling NaCl solution lowers the solution pH with concurrent formation of  $\text{Fe}_3\text{O}_4$ , thus accelerating corrosive processes.

## Naval Research Laboratory

## OXIDE FILM EFFECTS IN STRESS-CORROSION CRACKING

M. C. Bloom\* and S. H. Smith, Jr.

(\* Retired 1 July 1969)

## Objective

To determine whether the presence or absence of an oxide film on a metal alters its SCC behavior and whether the electrical conductivity or some other physical or electrochemical property of the oxide is a factor.

## Approach

Some suitable SCC evaluation test having been selected, a specimen would be coated with either conductive or insulating oxide and tested. Expected to be of importance would be porosity of the film and its dependence on the method of growth. Ease of hydrogen permeation might be germane too.

## Achievements

A procedure was devised for preparing type 4340 steel specimens for cantilever beam tests, but it was necessary to start the required fatigue crack before heat treating and this impeded experimental control of oxide in the crack. Instead, the simpler U-bend technique was put to use.

Experiments have thus far shown no performance difference between conductive ( $\text{Fe}_3\text{O}_4$ ) film coatings and insulating ( $\text{MnFe}_2\text{O}_4$ ) ones, but these were porous films. Other specimens coated with Teflon to simulate the physical but not chemical presence of oxide have tended to crack where pits formed at the bottom of pores. Iron plating 0.002 to 0.030-in.-thick curtails SCC in either acid (pH 2-3) or alkaline (pH 6-9) media, but oxidation of this plate to  $\text{Fe}_3\text{O}_4$  hastens it.

## Naval Research Laboratory

## SURFACE CHEMICAL STUDIES OF METAL SURFACES

L. B. Lockhart, Jr., and R. L. Patterson, Jr.

## Objective

Radiochemical techniques are used to investigate the nature of the bonding between adsorbed molecules and active sites at the surface of ferrous metals and their alloys.

## Approach

Adsorption/desorption studies are made of carbon-14-labeled stearic acid and octadecylamine on iron, steel, and glass surfaces to learn more about the extent of surface coverage, the effective surface area of highly polished surfaces, and the number and type of active adsorption sites present in the surface layer. Fire-polished soft glass is used as a reference surface.

## Achievements

Procedures have been developed for the preparation of condensed monomolecular films of stearic acid-1-C<sup>14</sup> on both soda-lime glass and ferrous metals using retraction from nitrobenzene solution. Desorption studies have shown that 20-40% of the adsorbed molecules are strongly bonded, presumably through chemical reaction with active surface sites. A relationship has been developed between the extent of surface coverage and the contact angle of the adsorbed film.

## Publications

"A Study of the Adsorption of Carbon-14 Labeled Stearic Acid on Iron," C. O. Timmons, R. L. Patterson, Jr., and L. B. Lockhart, Jr., NRL Report 6553, June 2, 1967; also J. Colloid and Interface Sci. 26, Jan 1968, pp. 120-127

"The Adsorption of Carbon-14-Labeled Stearic Acid on Soda-Lime Glass," R. L. Patterson, Jr. and L. B. Lockhart, Jr., NRL Report 6901, May 23, 1969

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